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# PATENT ABSTRACTS OF JAPAN

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## (54) HARD MAGNETIC MATERIAL

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a hard magnetic material, the cost of which is reduced and which has superior hard magnetic characteristics and superior temperature characteristic.

SOLUTION: A hard magnetic material, which consists of an alloy containing one or more kinds of elements T in Fe, Co and Ni, elements R composed of one or more kinds in rare earth elements, and B in which absolute value of temperature coefficient of magnetization is 0.15%/K or less, at a time when the material is used on the condition that a permeance coefficient reaches 2 or more, coercive force reaches 1 kOe or more, and the absolute value of the temperature coefficient of the coercive force reaches 0.35%/K or less, is adopted.

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**CLAIMS**

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[Claim(s)]

[Claim 1] A hard magnetic material characterized by for absolute values of a temperature coefficient of magnetization when using it in a configuration from which it consists of an alloy containing one or more sorts of elements T of Fe, Co, and the nickel and elements R and B which consist of one or more sorts in rare earth elements, and a permeance coefficient becomes two or more being below 0.15% / K, and coercive force being 1 or more kOes.

[Claim 2] A hard magnetic material characterized by for absolute values of a temperature coefficient of magnetization when using it in a configuration from which it consists of an alloy which contains a software magnetism phase of 1 or less kOe of coercive force or a semi- hard magnetism phase, and a hard magnetism phase of 1 or more kOes of coercive force more than 10vol(s)(volume) %, respectively, and a permeance coefficient becomes two or more being below 0.15% / K, and coercive force being 1 or more kOes.

[Claim 3] A hard magnetic material characterized by for absolute values of a temperature coefficient of magnetization when using it in a configuration from which Curie temperature consists of an alloy with which a magnetic phase and Curie temperature of 600 degrees C or more contain a magnetic phase of 600 degrees C or less more than 10vol(s)(volume) %, respectively, and a permeance coefficient becomes two or more being below 0.15% / K, and coercive force being 1 or more kOes.

[Claim 4] A hard magnetic material characterized by consisting of an alloy containing one or more sorts of elements T of Fe, Co, and the nickel, and elements R and B which consist of one or more sorts in rare earth elements, for absolute values of a temperature coefficient of coercive force being below 0.35% / K, and coercive force being 1 or more kOes.

[Claim 5] A hard magnetic material characterized by consisting of an alloy which contains a software magnetism phase of 1 or less kOe of coercive force, and a hard magnetism phase of 1 or more kOes of coercive force more than 10vol(s)(volume) %, respectively, for absolute values of a temperature coefficient of coercive force being below 0.35% / K, and coercive force being 1 or more kOes.

[Claim 6] A hard magnetic material characterized by for Curie temperature consisting of an alloy with which a magnetic phase and Curie temperature of 600 degrees C or more contain a magnetic phase of 600 degrees C or less more than 10vol(s)(volume) %, respectively, for absolute values of a temperature coefficient of coercive force being below 0.35% / K, and coercive force being 1 or more kOes.

[Claim 7] A hard magnetic material according to claim 1 to 6 characterized by including a fine crystalline phase of 100nm or less of diameters of average crystal grain as a main phase.

[Claim 8] A hard magnetic material according to claim 1 to 7 characterized by being the thing which comes to heat-treat an alloy which makes the main phase an amorphous phase which quenched an alloy molten metal and was obtained.

[Claim 9] A hard magnetic material according to claim 1 to 8 characterized by an alloy which makes the main phase an amorphous phase which quenched an alloy molten metal and was obtained being the thing which it comes to heat-treat with the above programming rate by 10K/in a temperature requirement where a first phase of a crystalline substance phase deposits at least.

[Claim 10] A hard magnetic material according to claim 1 to 9 characterized by an absolute value of a temperature coefficient of magnetization when using it in a configuration from which a permeance

coefficient becomes two or more being as follows [ 0.10% / K ].

[Claim 11] A hard magnetic material according to claim 1 to 10 characterized by an absolute value of a temperature coefficient of magnetization when using it in a configuration from which a permeance coefficient becomes ten or more being as follows [ 0.08% / K ].

[Claim 12] A hard magnetic material according to claim 1 to 11 characterized by absolute values of a temperature coefficient of coercive force in a 100-degree C temperature requirement being below 0.30% / K from a room temperature.

[Claim 13] A hard magnetic material according to claim 1 to 12 characterized by coercive force being the thing of 2 or more kOes.

[Claim 14] A hard magnetic material according to claim 1 to 13 characterized by being [ of residual magnetization (Ir) to saturation magnetization (Is) ] 0.6 or more things comparatively (Ir/Is).

[Claim 15] A hard magnetic material according to claim 1 to 14 which is expressed with the following empirical formula and characterized by residual magnetization (Ir) being the thing of 100 or more emu/g. While TxMyRzBw, however T express one or more sorts of elements among Fe, Co, and nickel, M expresses one or more sorts of elements among Zr, Nb, Ta, Hf, Ti, V, Mo, and W and R expresses one or more sorts of elements among rare earth elements x which shows a presentation ratio, and y, z and w are atomic %, and are  $50 \leq x$ ,  $0 \leq y \leq 15$ ,  $3 \leq z \leq 20$ , and  $2 \leq w \leq 20$ .

[Claim 16] x which shows a presentation ratio in said empirical formula, and y, z and w are a hard magnetic material according to claim 15 characterized by being atomic % and being  $80 \leq x \leq 93$ ,  $1 \leq y \leq 5$ ,  $3 \leq z \leq 10$ , and  $3 \leq w \leq 7$ .

[Claim 17] x which shows a presentation ratio in said empirical formula, and y, z and w are a hard magnetic material according to claim 15 characterized by being atomic % and being  $86 \leq x \leq 93$ ,  $1 \leq y \leq 3$ ,  $3 \leq z \leq 7$ , and  $3 \leq w \leq 5$ .

[Claim 18] x which shows a presentation ratio in said empirical formula, and y, z and w are a hard magnetic material according to claim 15 characterized by being atomic % and being  $x = 100 - y - z - w$ ,  $1 \leq y \leq 3$ ,  $3 \leq z \leq 7$ , and  $3 \leq w \leq 5$ .

[Claim 19] A hard magnetic material according to claim 1 to 14 characterized by what is expressed with the following empirical formula.

TxMyRzBwEv, however T express one or more sorts of elements among Fe, Co, and nickel. M expresses one or more sorts of elements among Zr, Nb, Ta, Hf, Ti, V, Mo, and W. While R expresses one or more sorts of elements among rare earth elements and E expresses one or more sorts of elements among Cr, aluminum, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, and germanium x which shows a presentation ratio, and y, z, w and v are atomic %, and are  $50 \leq x$ ,  $0 \leq y \leq 15$ ,  $3 \leq z \leq 20$ ,  $2 \leq w \leq 20$ , and  $0 \leq v \leq 10$ .

[Claim 20] x which shows a presentation ratio in said empirical formula, and y, z, w and v are a hard magnetic material according to claim 19 characterized by being atomic % and being  $80 \leq x \leq 93$ ,  $1 \leq y \leq 5$ ,  $3 \leq z \leq 10$ ,  $3 \leq w \leq 7$ , and  $0 \leq v \leq 5$ .

[Claim 21] x which shows a presentation ratio in said empirical formula, and y, z, w and v are a hard magnetic material according to claim 19 characterized by being atomic % and being  $x = 100 - y - z - w - v$ ,  $1 \leq y \leq 3$ ,  $3 \leq z \leq 7$ ,  $3 \leq w \leq 5$ , and  $0.1 \leq v \leq 5$ .

[Claim 22] x which shows a presentation ratio in said empirical formula, and y, z, w and v are a hard magnetic material according to claim 19 characterized by being atomic % and being  $86 \leq x \leq 93$ ,  $1 \leq y \leq 3$ ,  $3 \leq z \leq 7$ ,  $3 \leq w \leq 5$ , and  $0.1 \leq v \leq 5$ .

[Claim 23] A hard magnetic material characterized by coming to carry out 0.5- pentatomic % addition of the Si in T element substitute in a hard magnetic material according to claim 1 to 22.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the hard magnetic material in which was excellent in the magnetic engine performance which can be used for a magnetic type encoder, a potentiometer, a sensor, a motor, an actuator, a loudspeaker, etc., and the temperature characteristic was moreover excellent.

[0002]

[Description of the Prior Art] As a hard magnetic material which generally has the engine performance superior to a ferrite magnet or an alnico magnet (A1-nickel-Co-Fe system magnet), the Sm-Co system magnet, the Nd-Fe-B system magnet, etc. are known, and also many researches of an alloy magnet with a new Sm-Fe-N system magnet etc. are also made aiming at the high engine performance.

[0003]

[Problem(s) to be Solved by the Invention] However, these hard magnetic materials had the technical problem that a manufacturing cost will become high rather than a ferrite magnet or an alnico magnet since there is much amount of the expensive rare earth elements used, including Nd more than 10 atom %, or Sm more than 8 atom %. Moreover, since a Nd-Fe-B system magnet had a large change of the magnetic properties by temperature, it had the technical problem that it could not be used as a component of a sensor. Moreover, although the Sm-Co system magnet was a magnet with the small absolute value of the temperature coefficient of magnetization, since it was a magnet more expensive than a Nd-Fe-B system magnet, the range which can be used was restricted. On the other hand, although the manufacturing cost was low compared with the magnet with which a ferrite magnet contains rare earth elements as mentioned above, since the absolute value of the temperature coefficient of magnetization was large, the technical problem that it could not be used as a component of a sensor occurred. Moreover, the absolute value of the alnico magnet (A1-nickel-Co-Fe system magnet) of the temperature coefficient of magnetization was small, and although the manufacturing cost was low, since coercive force was small, it was difficult [ alnico magnet ] to use. For this reason, it had \*\*\*\*\* more than a ferrite magnet at least by low cost, and an appearance of the hard magnetic material in which the temperature characteristic was further excellent was desired.

[0004] Then, invention-in-this-application persons are performing patent application in Japanese Patent Application No. No. 68822 [ eight to ], Japanese Patent Application No. 8-242356, etc., in order to obtain the hard magnetic material which shows high \*\*\*\*\* by low cost. The element M which according to the technology indicated by such patent application uses Fe as a principal component and consists of one sort or two sorts or more in Zr, Nb, Ta, Hf, Ti, V, Mo, and W After producing the amorphous alloy containing the elements R and B which consist of one sort in rare earth elements, or two sorts or more using a melt quenching method, this amorphous alloy is heat-treated at 600-900 degrees C. By depositing the fine crystal phase of 100nm or less of diameters of average crystal grain which make a subject Fe of bcc, and the compound of Fe-B and/or R<sub>2</sub>Fe 14B1 The hard magnetic material 170 - 300 kA/m and the maximum magnetic energy product ((BH) max) indicate [ residual magnetization (Ir) / 0.8-1.3T, and coercive force (iHc) ] the comparatively high \*\*\*\*\* of 60 - 110 kJ/m<sup>3</sup> to be can be manufactured. By the radical of research of the above alloys, invention-in-this-application persons were low cost, in order to manufacture

the hard magnetic material in which \*\*\*\*\* was excellent in and the temperature characteristic was moreover excellent, as a result of repeating various examination and experiments, discovered that a permeance coefficient ( $\mu$ ) and the temperature coefficient of magnetization had correlation, and reached this invention.

[0005] This invention was made in view of the above-mentioned situation, is low cost and aims at offering the hard magnetic material in which \*\*\*\*\* was excellent in and the temperature characteristic was moreover excellent.

[0006]

[Means for Solving the Problem] The following configurations were used for this invention in order to solve an above-mentioned technical problem. Absolute values of a temperature coefficient of magnetization when using it in a configuration from which it consists of an alloy containing one or more sorts of elements T of Fe, Co, and the nickel and the elements R and B which consist of one or more sorts in rare earth elements, and a permeance coefficient becomes two or more are below  $0.15\% / K$ , and a hard magnetic material of this invention is characterized by coercive force being 1 or more kOes. Moreover, absolute values of a temperature coefficient of magnetization when using it in a configuration from which it consists of an alloy which contains a soft magnetic phase of 1 or less kOe of coercive force or a semi-hard magnetic phase, and a hard magnetic phase of 1 or more kOes of coercive force more than  $10\text{vol(s)}(\text{volume})\%$ , respectively, and a permeance coefficient becomes two or more are below  $0.15\% / K$ , and a hard magnetic material of this invention is characterized by coercive force being 1 or more kOes. Furthermore, absolute values of a temperature coefficient of magnetization when using it in a configuration from which Curie temperature consists of an alloy with which a magnetic phase and Curie temperature of 600 degrees C or more contain a magnetic phase of 600 degrees C or less more than  $10\text{vol(s)}(\text{volume})\%$ , respectively, and a permeance coefficient becomes two or more are below  $0.15\% / K$ , and a hard magnetic material of this invention is characterized by coercive force being 1 or more kOes.

[0007] It consists of an alloy which contains one or more sorts of elements T, and the elements R and B which consist of one or more sorts in rare earth elements among Fe, Co, and nickel, absolute values of a temperature coefficient of coercive force are below  $0.35\% / K$ , and a hard magnetic material of this invention is characterized by coercive force being 1 or more kOes. Moreover, it consists of an alloy which contains a soft magnetic phase of 1 or less kOe of coercive force, and a hard magnetic phase of 1 or more kOes of coercive force more than  $10\text{vol(s)}(\text{volume})\%$ , respectively, absolute values of a temperature coefficient of coercive force are below  $0.35\% / K$ , and a hard magnetic material of this invention is characterized by coercive force being 1 or more kOes. Furthermore, Curie temperature consists of an alloy with which a magnetic phase and Curie temperature of 600 degrees C or more contain a magnetic phase of 600 degrees C or less more than  $10\text{vol(s)}(\text{volume})\%$ , respectively, absolute values of a temperature coefficient of coercive force are below  $0.35\% / K$ , and a hard magnetic material of this invention is characterized by coercive force being 1 or more kOes.

[0008] A hard magnetic material of this invention is a hard magnetic material of a publication previously, and is characterized by including a fine crystalline phase of 100nm or less of diameters of average crystal grain as a main phase. Moreover, a hard magnetic material of this invention is a hard magnetic material of a publication previously, and is characterized by being the thing which comes to heat-treat an alloy which makes the main phase an amorphous phase which quenched an alloy molten metal and was obtained. Furthermore, a hard magnetic material of this invention is a hard magnetic material of a publication previously, and is characterized by an alloy which makes the main phase an amorphous phase which quenched an alloy molten metal and was obtained being the thing which it comes to heat-treat with the above programming rate by 10K/in a temperature requirement where a first phase of a crystalline substance phase deposits at least.

[0009] A hard magnetic material of this invention is a hard magnetic material of a publication previously, and is characterized by an absolute value of a temperature coefficient of magnetization when using it in a configuration from which a permeance coefficient becomes two or more being as follows  $[0.10\% / K]$ . Moreover, a hard magnetic material of this invention is a hard magnetic material of a publication previously,

and is characterized by an absolute value of a temperature coefficient of magnetization when using it in a configuration from which a permeance coefficient becomes ten or more being as follows [ 0.08% / K ]. Moreover, a hard magnetic material of this invention is a hard magnetic material of a publication previously, It is characterized by absolute values of a temperature coefficient of coercive force in a 100-degree C temperature requirement being below 0.30% / K from a room temperature. Furthermore, a hard magnetic material of this invention is a hard magnetic material of a publication previously, and is characterized by coercive force being the thing of 2 or more kOes. Furthermore, a hard magnetic material of this invention is a hard magnetic material of a publication previously, and is characterized by being [ of residual magnetization (Ir) to saturation magnetization (Is) ] 0.6 or more things comparatively (Ir/Is) again.

[0010] A hard magnetic material of this invention is a hard magnetic material of a publication previously, has the following empirical formula and is characterized by residual magnetization (Ir) being the thing of 100 or more emu/g.

While TxMyRzBw, however T express one or more sorts of elements among Fe, Co, and nickel, M expresses one or more sorts of elements among Zr, Nb, Ta, Hf, Ti, V, Mo, and W and R expresses one or more sorts of elements among rare earth elements x which shows a presentation ratio, and y, z and w are atomic %s, and are  $50 \leq x$ ,  $0 \leq y \leq 15$ ,  $3 \leq z \leq 20$ , and  $2 \leq w \leq 20$ .

[0011] Furthermore, it is desirable that it is  $x=100-y-z-w$ ,  $1 \leq y \leq 5$ ,  $3 \leq z \leq 10$ , and  $3 \leq w \leq 7$  at x which shows a presentation ratio in the above-mentioned empirical formula, y, z and w, and \*\*\*\*\* %, and it is still more desirable in the presentation range x of Element T being  $80 \leq x \leq 93$ . Furthermore, x which shows a presentation ratio in the above-mentioned empirical formula, and y, z and w are atomic %s, and it is desirable that it is  $x=100-y-z-w$ ,  $1 \leq y \leq 3$ ,  $3 \leq z \leq 7$ , and  $3 \leq w \leq 5$  again.

[0012] Moreover, a hard magnetic material of this invention is a hard magnetic material of a publication previously, and is characterized by being what has the following empirical formula.

TxMyRzBwEv, however T express one or more sorts of elements among Fe, Co, and nickel. M expresses one or more sorts of elements among Zr, Nb, Ta, Hf, Ti, V, Mo, and W. While R expresses one or more sorts of elements among rare earth elements and E expresses one or more sorts of elements among Cr, aluminum, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, and germanium x which shows a presentation ratio, and y, z, w and v are atomic %s, and are  $50 \leq x$ ,  $0 \leq y \leq 15$ ,  $3 \leq z \leq 20$ ,  $2 \leq w \leq 20$ , and  $0 \leq v \leq 10$ .

[0013] Furthermore, x which shows a presentation ratio in the above-mentioned empirical formula, and y, z, w and v are atomic %s, and it is desirable that it is  $80 \leq x \leq 93$ ,  $1 \leq y \leq 5$ ,  $3 \leq z \leq 10$ ,  $3 \leq w \leq 7$ , and  $0 \leq v \leq 5$ . Furthermore, it is more desirable that x which shows a presentation ratio in the above-mentioned empirical formula, and y, z, w and v are atomic %s, and it is  $x=100-y-z-w-v$ ,  $1 \leq y \leq 3$ ,  $3 \leq z \leq 7$ ,  $3 \leq w \leq 5$ , and  $0.1 \leq v \leq 5$  again, and it is still more desirable when the presentation range x of Element T sets to  $86 \leq x \leq 93$ . Moreover, if 0.5- pentatomic % addition of Si is done in T element substitute, since \*\*\*\*\* of a hard magnetic material concerning this invention will improve, it is more desirable.

[0014]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained in detail. The absolute values of the temperature coefficient of the magnetization when using it in the configuration from which the hard magnetic material of this invention consists of an alloy which contains one or more sorts of elements T and the elements R and B which consist of one or more sorts in rare earth elements among Fe, Co, and nickel, and a permeance coefficient becomes two or more are below 0.15% / K, and coercive force is 1 or more kOes. Moreover, the hard magnetic material of this invention consists of an alloy which contains one or more sorts of elements T, and the elements R and B which consist of one or more sorts in rare earth elements among Fe, Co, and nickel, the absolute values of the temperature coefficient of coercive force are below 0.35% / K, and coercive force is 1 or more kOes.

[0015] The property of a magnet material is expressed by the portion of the 2nd quadrant of a hysteresis curve, i.e., a demagnetization curve. Since the magnet material after magnetization is the magnetic field of the reverse sense which own residual magnetization builds, and under an anti-magnetic field, the operating point (the flux density (B) and the demagnetizing field (H) of a material) is given by one point p on a demagnetization curve. The line (OP) between a permeance coefficient (p), and p and Zero O is called a



permeance line for the value (non-dimensionality) of  $B/\mu_0 H$  here. If this permeance coefficient ( $p$ ) or a permeance line becomes small if magnetization lay length becomes short depending on a magnetic configuration, and it becomes long, it becomes large, and the thing of  $p=1.5$  is a disc form, for example, the thing of  $p=10$  is a prism form. Between a permeance coefficient ( $p$ ) and a demagnetization factor ( $N$ ), it is the following type (1).

$$p = (1-N) / N \dots (1)$$

It comes out and there is relation shown. Therefore, if the configurations of a demagnetization curve and a magnet material are given, the operating point ( $B, H$ ) will be determined. The energy ( $U$ ) of a static magnetic field which the magnet material builds outside is the following type (2).

$$U = BHV/2 \dots (2)$$

(—  $V$  is given by volume) of a magnetic material among a formula. If the configuration of a magnet material changes, since an anti-magnetic field, i.e., a permeance line, will change, the operating point  $p$  changes and the value of Above  $U$  changes. The value of  $U$  serves as max in a certain operating point  $p_m$  the middle, and the product of  $(BH)$  at that time is the maximum magnetic energy product  $((BH)_{\max})$ .

[0016] In order to prevent that originate in a temperature change and a drift arises in an output when using the hard magnetic material concerning this invention for a sensor etc., it is desirable to use the thing, i.e., what, has the small absolute value of the temperature coefficient of magnetization and in which the temperature characteristic is excellent, and below  $0.15\% / K$ , since the absolute value of the temperature coefficient of the magnetization when using it in the configuration from which a permeance coefficient becomes two or more as mentioned above is small, it can use the hard magnetic material of this invention for a sensor etc. Moreover, when a value with a small permeance coefficient, for example, a permeance coefficient, uses the hard magnetic material concerning this invention in two or less configuration, it is set. Since the \*\*\*\*\* of a hard magnetic material is influenced by the temperature coefficient of coercive force rather than the temperature coefficient of magnetization, it is desirable to use what has the small temperature coefficient of coercive force. The hard magnetic material of this invention As mentioned above, below  $0.35\% / K$ , with  $0.30\% / K$ , since the absolute value of the temperature coefficient of coercive force is small, it can use it for a small sensor etc. especially in the temperature requirement in which it is room temperature  $-100$  degree C. Moreover, as for the hard magnetic material of this invention, what the absolute value of the temperature coefficient of the magnetization when using it in a configuration from which a permeance coefficient becomes two or more becomes below  $0.10\% / K$  is more desirable at the point that the temperature characteristic is more excellent. Furthermore, as for the hard magnetic material of this invention, it is more desirable to use it in a configuration from which a permeance coefficient becomes ten or more at the point that the absolute value of the temperature coefficient of magnetization is more excellent in the temperature characteristic below  $0.08\% / K$ .

[0017] Below  $0.15\% / K$ , the absolute value of the temperature coefficient of the magnetization when using the hard magnetic material of this invention in the configuration from which a permeance coefficient becomes two or more is more preferably equivalent to below  $0.10\% / K$ , and a conventional-type Nd-Fe-B system magnet, or can realize a thing smaller than it. Furthermore, the hard magnetic material of this invention is cheaper than the Sm-Co system magnet with which the temperature characteristic is used as a good thing from the former greatly [ coercive force ( $iH_c$ ) ] from the alnico magnet. Moreover, the absolute value of the temperature coefficient of magnetization when the absolute value of the temperature coefficient of the magnetization when using the magnet of the conventional Nd-Fe-B system in the configuration from which a permeance coefficient becomes ten or more uses [ a permeance coefficient ] the hard magnetic material of this invention to  $0.11 - 0.15\% / K$  in the configuration which becomes ten or more can realize below  $0.08\% / K$ , and a small thing. Furthermore, as for the hard magnetic material of this invention, the absolute value of the temperature coefficient of coercive force can realize a small thing below  $0.35\% / K$  to the absolute values of the temperature coefficient of the coercive force of the magnet of the conventional Nd-Fe-B system being  $0.35 - 0.4\% / K$ . Especially, the absolute value of the temperature coefficient of the coercive force in a room temperature  $-100$  degree C temperature requirement can be made small below  $0.30\% / K$ . Especially the hard magnetic material of this invention can realize suitably the

hard magnetic material excellent in the temperature characteristic by Co being made to be contained in 0.5 – pentatomic % addition or T element in T element substitute 0.5 to 20% about Si so that it may mention later.

[0018] Moreover, the coercive force (iHc) of the hard magnetic material of this invention may be the thing of 1 or more kOes more than 10vol(s)(volume) %, including respectively the software magnetism phase of 1 or less kOe of coercive force or a semi- hard magnetism phase, and the hard magnetism phase of 1 or more kOes of coercive force. Thus, when the software magnetism phase of 1 or less kOe of coercive force or the semi- hard magnetism phase, and the hard magnetism phase of 1 or more kOes of coercive force are included in the above-mentioned range, it is desirable at the point which can be equipped with each property of a software magnetism phase and a hard magnetism phase. Since Nd required for a hard magnetism phase etc. increases that the software magnetism phase of 1 or less kOe of coercive force or a semi- hard magnetism phase is under 10vol(s)(volume) % and residual magnetization (Ir) falls, it is not desirable. Moreover, since coercive force (iHc) becomes it low that the hard magnetism phase of 1 or more kOes of coercive force is under 10vol(s)(volume) %, it is not desirable. The content with desirable software magnetism phase of 1 or less kOe of coercive force or semi- hard magnetism phase is 20–60vol(volume) %, and the content with the desirable hard magnetism phase of 1 or more kOes of coercive force is 40–80vol(volume) %.

[0019] Furthermore, the absolute values of the temperature coefficient of coercive force may be below 0.35% / K more than 10vol(s)(volume) %, including respectively the software magnetism phase of 1 or less kOe of coercive force, and the hard magnetism phase of 1 or more kOes of coercive force, and the coercive force of the hard magnetic material of this invention may be the thing of 1 or more kOes. Thus, if the software magnetism phase of 1 or less kOe of coercive force and the hard magnetism phase of 1 or more kOes of coercive force are included in the above-mentioned range, it can have each property of a software magnetism phase and a hard magnetism phase like \*\*\*\*.

[0020] Moreover, coercive force may be the thing of 1 or more kOes, including respectively the magnetic phase of 600 degrees C or less more than 10vol(s)(volume) %, and the hard magnetic material of this invention has [ the magnetic phase and Curie temperature of 600 degrees C or more ] a Curie temperature desirable at the point that Curie temperature can have each property of a software magnetism phase and a hard magnetism phase if the magnetic phase and Curie temperature of 600 degrees C or more contain the magnetic phase of 600 degrees C or less in the above-mentioned range, in this way. Since the Curie temperature of a bcc-Fe phase is near 770 degree C and the Curie temperature of R2Fe14 B phase is near 315 degree C, in order for it to have two phases of the software magnetism phase and hard magnetism phase to which the hard magnetic material of this invention participates in magnetization and which are a phase, the magnetic phase and Curie temperature of 600 degrees C or more need to contain [ Curie temperature ] the magnetic phase of 600 degrees C or less. Since the temperature change of the magnetization when using that it is under 10vol(s)(volume) % by the comparatively high permeance becomes large, the magnetic phase of 600 degrees C or more does not have a desirable Curie temperature. Moreover, since a hard magnetism phase decreases that Curie temperature is [ the magnetic phase of 600 degrees C or less ] under 10vol(s)(volume) %, coercive force (iHc) becomes low and is not desirable. The Curie temperature of a desirable content with a magnetic phase of 600 degrees C or more is 20–60vol(volume) %, and the Curie temperature of a desirable content with a magnetic phase of 600 degrees C or less is 40–80vol(volume) %.

[0021] Moreover, the hard magnetic material of this invention contains the fine crystalline phase of 100nm or less of diameters of average crystal grain as a subject, and the bcc-Fe phase of 100nm or less of diameters of average crystal grain and the R2Fe14 B phase of 100nm or less of diameters of average crystal grain deposit in this fine crystalline phase. Furthermore, the hard magnetic material of this invention forms the nano diplophase organization of the above-mentioned bcc-Fe phase, the fine crystalline phase of R2Fe14 B phase, and the amorphous phase that remained. Moreover, you may come to heat-treat the alloy which makes the main phase the amorphous phase obtained when the hard magnetic material of this invention quenched the alloy molten metal of the above-mentioned configuration. It is desirable that the

alloy which makes the main phase the amorphous phase which quenched the alloy molten metal of the above-mentioned configuration, and was obtained especially is the thing which it comes to heat-treat with the above programming rate by 10K/in the temperature requirement where the first phase of a crystalline substance phase deposits at least at the point which makes fine mean particle diameter of a bcc-Fe phase, and raises \*\*\*\*\*. Many of hard magnetic materials of this invention are the so-called first phases in which a bcc-Fe phase, Fe<sub>3</sub>B phase, or Fe<sub>2</sub>B phase deposits by heat treatment earlier than other phases (R<sub>2</sub>Fe<sub>14</sub>B phase).

[0022] Furthermore, as for the hard magnetic material concerning this invention, it is desirable that coercive force (iH<sub>c</sub>) is the thing of 2 or more kOes. Moreover, as for the hard magnetic material concerning this invention, it is desirable that they are [ of the residual magnetization (I<sub>r</sub>) to saturation magnetization (I<sub>s</sub>) ] 0.6 or more things comparatively (I<sub>r</sub>/I<sub>s</sub>). Here, the value of the magnetization which is obtained when saturation magnetization (I<sub>s</sub>) applies the magnetic field of 15 or more kOes to a sample in this invention and which was saturated mostly is meant. Control of the diameter of average crystal grain of the crystalline substance phase in the above hard magnetic materials and the concentration of each atom in each phase is realizable by controlling the heat treatment conditions at the time of heat-treating the alloy which makes an amorphous substance the main phase, and obtaining a hard magnetic material. Heat treatment conditions are a programming rate, heat treatment temperature (annealing temperature), its holding time, etc.

[0023] The hard magnetic material concerning this invention can be expressed with the following empirical formulas.

Although T in the TxMyRzBw above-mentioned empirical formula is the remainder which deducted the content of Elements M, R, and B from the whole fundamentally, it expresses one or more sorts of elements among Fe, Co, and nickel. Since these elements T are the principal components of the hard magnetic material concerning this invention and it is the element which bears magnetism, the presentation ratio x of Element T is more than 50 atom %. If the presentation ratio x of Element T is made to increase, saturation magnetization (I<sub>s</sub>) will increase in connection with it. In order to realize high residual magnetization (I<sub>r</sub>) of 100 or more emu/g, 130 emu/g at least needs saturation magnetization (I<sub>s</sub>), for filling this, as for the presentation ratio x of Element T, it is desirable that it is more than 80 atom %, and it is more desirable that it is more than 86 atom %. Moreover, in order to obtain good \*\*\*\*\*, it is desirable to carry out to below 93 atom %. In the hard magnetic material of this invention, it is required to contain Fe as some elements [ at least ] T.

[0024] M in the above-mentioned empirical formula expresses one or more sorts of elements among Zr, Nb, Ta, Hf, Ti, V, Mo, and W, and these elements M have high amorphous organization potency. In the hard magnetic material concerning this invention, by adding Element M, even when Element R (rare earth elements) is low concentration, an amorphous phase can be formed. If the presentation ratio y of Element M is made to increase in element R substitute, although residual magnetization (I<sub>r</sub>) increases in connection with it, coercive force (iH<sub>c</sub>) will decline and it will change from \*\*\*\*\* to soft magnetic characteristics. Moreover, if Element M is made to increase in the element T substitute which bears magnetism, reduction of saturation magnetization (I<sub>s</sub>) and residual magnetization (I<sub>r</sub>) will arise. Therefore, in order to obtain good \*\*\*\*\*, as for the presentation ratio y of Element M, it is desirable to consider as the range below 15 atom % more than 0 atom %, and it is more desirable that it is a range below pentatomic % more than 1 atom %. Moreover, it is still more desirable when it carries out to below 3 atom % more than 1 atom %.

[0025] R in the above-mentioned empirical formula expresses one or more sorts of elements of the rare earth elements (Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). Intermetallic-compound R<sub>2</sub>Fe<sub>14</sub>B which deposits when the alloy which makes the main phase the amorphous substance containing Element R, and Fe and B is heated at a suitable temperature of the range of 873–1173K (600–900 degrees C) gives \*\*\*\*\* excellent in the hard magnetic material of this invention. If the presentation ratio z of Element R is made to increase, saturation magnetization (I<sub>r</sub>) will decrease in connection with it. In order to obtain the high residual magnetization (I<sub>r</sub>) of 100 or more emu/g, 130 emu/g at least needs saturation magnetization (I<sub>s</sub>), and in order to fill this, as for the presentation ratio z of

Element R, it is desirable that it is below 20 atom %. Moreover, Element R is an element which is easy to form an amorphous substance, and in order for carrying out to more than 3 atom % as a presentation ratio z of Element R since a good amorphous phase or a fine crystal phase cannot be obtained if the presentation ratio z of Element R is too small to reconcile desirable and high saturation magnetization (Ir) and coercive force (iHc), it is good [ Element ] to carry out to below 7 atom % still more preferably below 10 atom %. If some or all of Element R is furthermore constituted from Nd and/or Pr, still higher \*\*\*\*\* will be obtained.

[0026] B in the above-mentioned empirical formula is an element which is easy to form an amorphous substance. Moreover, compound R<sub>2</sub>Fe<sub>14</sub>B which deposits when the amorphous phase containing Element R, and Fe and B is heat-treated at a suitable temperature of the range of 873–1173K (600–900 degrees C) gives \*\*\*\*\* to the hard magnetic material of this invention. In order to obtain a good amorphous phase or a fine crystalline phase, it is desirable to carry out concentration of B to more than 2 atom %, but since saturation magnetization (Is), residual magnetization (Ir), and coercive force (iHc) decrease with the increment in the presentation ratio w of B, in order to obtain good \*\*\*\*\*, it is desirable to make the presentation ratio w of B below into pentatomic % still more preferably below 7 atom % more preferably below 20 atom %.

[0027] Moreover, one or more sorts of elements E may be added by the hard magnetic material of this invention among Cr, aluminum, Pt, Ru, Rh, Pd, Os, Ir, Cu, Ag, Au, Ga, and germanium, and the hard magnetic material in that case can be expressed with the following empirical formula to it.

TxMyRzBwEv — the presentation ratio x of the element T which bears the magnetism in this case, although it is the remainder which deducted the content of Elements M, R, B, and E from the whole fundamentally It is a range below 93 atom % more than 80 atom % more preferably more than 50 atom % from the point to which saturation magnetization (Is) is made to increase. In order to realize coexistence of the high residual magnetization (Ir) of 100 or more emu/g, and high coercive force (iHc), it is desirable to consider as the range below 93 atom % more than 86 atom %. More than 0 atom %, below 15 atom %, more preferably, in order to realize high residual magnetization (Ir) of 100 or more emu/g, it is preferably [ in order to obtain good \*\*\*\*\* ] desirable [ the ratio / the presentation ratio y of the element M in the above-mentioned empirical formula is a range below pentatomic % more than 1 atom %, and ] to consider as the range below 3 atom % more than 1 atom %. In addition, in order to obtain higher residual magnetization (Ir), it is good also as below 1 atom % more than 0.5 atom % in a presentation ratio.

[0028] More than 3 atom %, below 20 atom %, more preferably, in order to realize high residual magnetization (Ir) of 100 or more emu/g, it is preferably [ in order to obtain an amorphous phase good in order to give \*\*\*\*\* excellent in the hard magnetic material of this invention, or a fine crystalline phase ] desirable [ the ratio / the presentation ratio z of the element R in the above-mentioned empirical formula is a range below 10 atom % more than 3 atom %, and ] to consider as 7% or less of range more than 3 atom %. In order to obtain a good amorphous phase or a fine crystalline phase, as for the presentation ratio w of B in the above-mentioned empirical formula, it is desirable to carry out to more than 2 atom %, but in order to obtain good \*\*\*\*\*, it is desirable to make the presentation ratio w of B below into pentatomic % still more preferably below 7 atom % more preferably below 20 atom %. The corrosion resistance of a hard magnetic material can promote improvement or detailed-ization of the crystalline structure by adding Element E. Therefore, as for the presentation ratio v of Element E, it is desirable that it is more than 0.1 atom %. However, since \*\*\*\*\* will deteriorate if the presentation ratio v of Element E is too high, the presentation ratio v of Element E is more preferably made below into pentatomic % below 10 atom %. Moreover, it is more desirable not to add Element E, in order to attain the high residual magnetization (Ir) of 100 or more emu/g.

[0029] In the hard magnetic material of this invention, if Co is made to be contained in Element T in addition to Fe, it is desirable at the point which can make small the absolute value of the temperature coefficient of the magnetization when using it in the absolute value of the temperature coefficient of the magnetization when using it in the configuration from which a permeance coefficient becomes two or more, and the configuration from which a permeance coefficient becomes ten or more, and the absolute value of

the temperature coefficient of coercive force. It is because the temperature change of magnetic properties becomes small, this Co is further contained also in a bcc-Fe phase, so the temperature change of residual magnetization becomes small since Curie temperature will rise if Co is contained in Element T, magnetization and the temperature change of coercive force become small and, as for that reason, the square shape ratio of magnetization becomes high. It is preferably [ more ] desirable [ contents ], since too many contents of Co will degrade magnetic properties if there are preferably to consider as the range below 20 atom % more than 0.5 atom % still more preferably, and to set up suitably according to a presentation, heat treatment conditions, etc. of an alloy below 30 atom % more than 0.5 atom % below 50 atom %.

[0030] Moreover, in the hard magnetic material of this invention, if Si is added in element T substitute, the absolute value of the temperature coefficient of the magnetization when using it in the absolute value of the temperature coefficient of the magnetization when using it in the configuration from which magnetic properties especially coercive force (iHc), and the maximum magnetic energy product ((BH) max) can be further raised, and a permeance coefficient becomes two or more, and the configuration from which a permeance coefficient becomes ten or more especially can be made low. Since the presentation ratio of Element T becomes low and the magnetic properties of a hard magnetic material will fall on the contrary if many [ too ], as for the addition of Si, it is preferably desirable to consider as the range below 3 atom % more than 0.5 atom % more preferably, and to set up suitably according to a presentation, heat treatment conditions, etc. of an alloy below pentatomic % more than 0.5 atom %. Thus, especially the hard magnetic material by which coercive force (iHc) and the temperature characteristic have been improved is suitably used as the magnet for small motors, and a sensor.

[0031] Next, the hard magnetic material concerning this invention can be manufactured as follows. The method by the melt quenching method, or sputtering and CVD methods, such as the method of spraying and quenching an alloy molten metal to a rotating drum, and forming in thin band-like one and the method of spouting an alloy molten metal in the gas for cooling, quenching in the state of a drop, and forming in the shape of powder, etc. can be used for the method of obtaining the alloy which makes the above amorphous substances the main phase. Moreover, when acquiring the consolidation object which can perform heat treatment to the alloy which makes the above-mentioned amorphous substance the main phase using the heating means of arbitration, for example, consists of a hard magnetic material of this invention, while making into the shape of powder the alloy which makes an amorphous substance the main phase first and carrying out pressing of the end of an alloy powder with a hotpress, the method of heat-treating at a suitable programming rate and heat treatment temperature (annealing temperature) can be used preferably.

[0032] By 10K/, above, the programming rate at the time of heat treatment is the above range by 100K/, and is preferably set up with the presentation of the alloy which makes an amorphous substance the main phase. The crystal grain which deposits in an alloy that the programming rate at the time of heat treatment is the following by 10K/by heat treatment makes it big and rough, and they are a software magnetism phase (bcc(body-centered cubic structure)-Fe) and a hard magnetism phase (R<sub>2</sub>Fe<sub>14</sub>B). Since a switched connection property falls and \*\*\*\*\* deteriorates, it is not desirable. Moreover, shortening of the time amount which the improvement in a property, heat treatment process, and manufacturing process by equalization of a detailed organization take is attained by making the programming rate at the time of heat treatment into the above range by 100K/. In addition, as a maximum of a programming rate, it may be about a 200K/minute from the constraint on equipment.

[0033] Further excellent \*\*\*\*\* is obtained by considering more preferably above the programming rate when heat-treating the alloy which makes an amorphous phase the main phase especially as the above by 50K/by 10K/in the temperature requirement where the first phase of a crystalline substance phase deposits at least. In the hard magnetic material concerning this invention, to the crystal phase which deposits by heat treatment, a bcc-Fe phase (software magnetism phase), The phase (first phase) which R<sub>2</sub>Fe<sub>14</sub>B (hard magnetism phase) and Fe<sub>3</sub> B phase are contained, and deposits at the lowest temperature among these crystal phases For example, it is a bcc-Fe phase, Fe<sub>3</sub> B phase, or Fe<sub>2</sub>B phase, and that temperature that deposits changes by this either becoming a first phase with presentations of the alloy

which makes an amorphous phase the main phase, for example, it is within the limits of 500–650 degrees C. Moreover, it is most desirable that a bcc-Fe phase deposits as a first phase. Since the switched connection property of a software magnetism phase (bcc(body-centered cubic structure)-Fe) and a hard magnetism phase (R2Fe14B) falls in order that the crystal grain of a bcc-Fe phase which deposits in an alloy that the programming rate in this temperature requirement is the following by 10K/by heat treatment may make it big and rough, and \*\*\*\*\* deteriorates, it is not desirable. Moreover, by making into the above range the programming rate in the temperature requirement where the first phase of a crystalline substance phase deposits by 50K/, it becomes possible to make detailed more particle size of the crystal grain of a bcc-Fe phase, and the crystal phase of a uniform detailed organization can be formed.

[0034] In the in-house of the alloy which makes an above-mentioned amorphous phase the main phase, the difference of the concentration of the fluctuation of an alloy presentation, i.e., an alloy presentation, is large. At the time of heat treatment, the first phase (bcc-Fe phase) of a crystal phase grows by using the portion of such fluctuation as a nucleus. If a programming rate is large at this time, origination-of-nucleus probability becomes high and many crystal grain of a bcc-Fe phase deposits by the alloy in-house. Since the diameter of crystal grain is dependent on a programming rate, the particle size of a bcc-Fe phase becomes so small that a programming rate is large. Furthermore, if temperature up is continued, R2Fe14 B phase begins to deposit from the portion of the grain boundary of a bcc-Fe phase. It is not necessary to necessarily carry out the programming rate at this time above by 10K/. Although the dependency of the programming rate of the particle size of R2Fe14 B phase is in the inclination for particle size to become small so that it is large and a programming rate is larger than the case of a bcc-Fe phase Since the volume which many crystal grain of a bcc-Fe phase has already deposited, and the crystal grain of the bcc-Fe phase under alloy organization occupies in this invention is large The space where R2Fe14 B phase deposits becomes small relatively, and even if the programming rate in the temperature requirement which deposits R2Fe14 B phase is the following by 10K/, the particle size of R2Fe14 B phase becomes small. That is, it depends for the particle size of R2Fe14 B phase on the programming rate in the temperature requirement where a first phase (bcc-Fe phase) deposits greatly. Thus, in the hard magnetic material in this invention, it is thought that it becomes the gestalt to which much crystal grain of R2Fe14 B phase deposited around the crystal grain of many bcc-Fe phases, the switched connection property of a bcc-Fe phase and R2Fe14 B phase improves, and \*\*\*\*\* improves.

[0035] The heat treatment temperature at the time of heat treatment (annealing temperature) is preferably set up with 873–1173K (600–900 degrees C), and the presentation of the alloy which it is more desirable, and the range of 973K–1023K (700–800 degrees C) and the holding time (heat treatment time amount) are desirable, is a range for 3 – 10 minutes more preferably for 0 to 60 minutes, and makes an amorphous phase the main phase. Since there are few amounts of deposits of the R2Fe14 B phase which bears \*\*\*\*\* as heat treatment temperature is under 873K (600 degrees C), sufficient \*\*\*\*\* is not obtained, and it is not desirable. On the other hand, if heat treatment temperature exceeds 1173K (900 degrees C), since other sludges will deposit and \*\*\*\*\* will fall, it is not desirable.

[0036] Drawing 1 is the perspective diagram showing the example of the operation gestalt which applied the hard magnetic material of this invention to the magnet for hole potentiometers. The magnet section which consists of a hard magnetic material concerning this invention with the above-mentioned sign 1 in drawing, and 2 are the supporters for supporting this magnet section 1. It is the sector thing by which the permeance coefficient was fabricated by the configuration which becomes about about five, the absolute values of the temperature coefficient of magnetization are below 0.13% / K, and the absolute value of the temperature coefficient of coercive force of the above-mentioned magnet section 1 is as follows [ 0.35% / K ]. The above-mentioned supporter consists of inlet connection 5 of the shape of a cylinder established by projecting from the disc section 4 which has the notching section 3 for containing the magnet section 1, and the crowning of this disc section 4.

[0037] or [ that the temperature characteristic is more equivalent than a conventional ferrite magnet and a conventional Nd-Fe-B system magnet by having used the magnet section 1 which consists of hard magnetic material nature concerning this invention if it was in the magnet for hole potentiometers of an

operation gestalt ] — or it excels, and since the drift of the output resulting from a temperature change can be prevented, it can adjust with a sufficient precision of the circuit voltage of electronic equipment. Moreover, if it is in the magnet for hole potentiometers of an operation gestalt, it is low cost from a conventional Sm-Co system magnet and a conventional Nd-Fe-B system magnet, and \*\*\*\*\* is superior to a conventional ferrite and a conventional alnico magnet.

[0038] Drawing 2 is the perspective diagram showing the example of the operation gestalt which applied the hard magnetic material of this invention to the magnet for magnetic type rotary encoders. The sign 10 in drawing is the magnet for magnetic type rotary encoders of an operation gestalt. The magnet 10 for magnetic type rotary encoders of this operation gestalt was fabricated by the configuration from which it consists of a hard magnetic material concerning above-mentioned this invention, and a permeance coefficient becomes about about two, and a multi-electrode comes [ disc-like ] to magnetize it in accordance with that periphery. Moreover, the absolute value of the temperature coefficient of magnetization of this magnet 10 for rotary encoders is as follows [  $0.15\% / K$  ]. or [ that the temperature characteristic is more equivalent than a conventional ferrite magnet and a conventional Nd-Fe-B system magnet by having used the hard magnetic material nature concerning this invention if it is in the magnet 10 for magnetic type rotary encoders of an operation gestalt ] — or it excels, and since the drift of the output resulting from a temperature change can be prevented, angle of rotation of electronic equipment etc. is detectable with a sufficient precision. Moreover, if it is in the magnet 10 for magnetic type rotary encoders of an operation gestalt, it is low cost from a conventional Sm-Co system magnet and a conventional Nd-Fe-B system magnet, and \*\*\*\*\* is superior to a conventional ferrite and a conventional alnico magnet.

[0039] Drawing 3 is the cross section showing the first example of the operation gestalt which applied the hard magnetic material of this invention to the magnet for loudspeakers. The pole piece which the sign 21 in drawing becomes from iron, the cylinder-like dust core (yoke) in which 22 was prepared by separating a crevice to the way outside this pole piece 21, the magnet with which 23 and 24 consist of a hard magnetic material of this invention by which the crevice between the pole piece 21 and a yoke 22 has been arranged up and down, respectively, and 25 are cone-like diaphragms. The above-mentioned magnets 23 and 24 are formed in the shape of a ring. The speech coil (graphic display abbreviation) is arranged between the magnetic gaps made with these magnets 23 and 24, and this speech coil is further connected to the cone-like diaphragm 25. If the speech current from amplifier flows to this speech coil, motion can be caused according to it, the cone-like diaphragm 25 connected to this can be moved, and it can emanate as a sound.

[0040] If it is in the magnet for loudspeakers of the first example, since the drift of the output in which the temperature characteristic excels a conventional ferrite magnet and a conventional Nd-Fe-B system magnet and which originates in a temperature change can be prevented by having used the magnets 23 and 24 which consist of hard magnetic material nature concerning this invention, speech current can be passed with a sufficient precision to a voice coil. Moreover, if it is in the magnet for loudspeakers of the first example, it is low cost from a conventional Sm-Co system magnet and a conventional Nd-Fe-B system magnet, and \*\*\*\*\* is superior to a conventional ferrite and a conventional alnico magnet.

[0041] Drawing 4 is the cross section showing the second example of the operation gestalt which applied the hard magnetic material of this invention to the magnet for loudspeakers. The pole piece which consists of iron of a vertical couple with which opposite arrangement of the signs 31 and 32 in drawing was carried out, the magnet which consists of a hard magnetic material of this invention by which 33 was arranged between this pole piece 31 and 32, the cylinder-like yoke with which 34 was prepared by separating a crevice to the way outside these pole piece 31 and 32 and a magnet 33, and 35 are cone-like diaphragms, and 36 is magnetic-shielding covering. The above-mentioned magnet 33 is formed in the shape of a ring. The above-mentioned pole piece 31 and 32 and a magnet 33 are attached in the magnetic-shielding covering 36 with the bolt 37, the washer 38, and the nut 39. If it is in the magnet for loudspeakers of the second example, there is the same effect as the magnet for loudspeakers of the first above-mentioned example and abbreviation by having used the magnet 33 which consists of hard magnetic material nature



concerning this invention.

[0042] Especially an above-mentioned hard magnetic material among Fe, Co, and nickel One or more sorts of elements T Since the absolute value of the temperature coefficient of the magnetization when using it in the configuration from which it consists of an alloy containing the elements R and B which consist of one or more sorts in rare earth elements, and a permeance coefficient becomes two or more is as follows [  $0.15\% / K$  ] or [ that the temperature characteristic is more equivalent than a conventional ferrite and a conventional Nd-Fe-B system magnet ] -- or since the drift of the output resulting from a temperature change can be prevented when it excels, therefore uses for a sensor etc., the reliability of detection precision can be raised. Moreover, although the temperature characteristic of a hard magnetic material is greatly influenced by the temperature coefficient of coercive force when it is used in a configuration from which a permeance coefficient becomes two or less Below  $0.35\% / K$ , since the absolute value of the temperature coefficient of coercive force is small, an above-mentioned hard magnetic material or [ that the temperature characteristic is more equivalent than the conventional Nd-Fe-B system magnet ] -- or since the drift of the output resulting from a temperature change can be prevented when it excels and is used for a small magnetometric sensor, a rotary encoder, etc., the reliability of detection precision can be raised.

[0043] The hard magnetic material concerning this invention contains the fine crystalline phase of 100nm or less of diameters of average crystal grain as a subject. Moreover, to this fine crystalline phase Since the bcc-Fe phase of 100nm or less of diameters of average crystal grain and the R2Fe14 B phase of 100nm or less of diameters of average crystal grain deposit The switched connection property of a software magnetism phase (bcc(body-centered cubic structure)-Fe) and a hard magnetism phase (R2Fe14B) is improving. Residual magnetization (Ir), a square shape ratio (Ir/Is), coercive force (iHc), and the maximum magnetic energy product ((BH) max) increase, and it is A. \*\*\*\*\* is obtained. Specifically, residual magnetization (Ir) can realize 100 or more emu/g of outstanding hard magnetic materials to which the hard magnetic material of 130 or more emu/g and a square shape ratio (Ir/Is) exceed [ the hard magnetic material of 2 or more kOes, and the maximum magnetic energy product ((BH) max) ] 0.7 or more hard magnetic materials, and coercive force (iHc) exceeds 1 or more kOe(s) of 100 kJ/m<sup>3</sup> 0.6 or more preferably.

[0044] Furthermore, since \*\*\*\*\* which was excellent even if it lessened the content of rare earth elements R is obtained, the hard magnetic material concerning this invention can be manufactured with a comparatively low manufacturing cost compared with an Sm-Co system magnet or a Nd-Fe-B system magnet.

[0045] Moreover, an above-mentioned hard magnetic material heat-treats the alloy which makes an amorphous phase the main phase immediately after quenching, and deposits a detailed crystal phase. When the programming rate at the time of heat-treating especially considers as the above by 10K/in the temperature requirement where the first phase of a crystalline substance phase deposits, while much crystal grain of a bcc-Fe phase can form and being able to prevent hypertrophy of the crystal grain Since hypertrophy of the crystal grain of the R2Fe14 B phase generated later can also be prevented, the diameter of average crystal grain of the bcc-Fe phase of a fine crystalline phase and R2Fe14 B phase which deposits in the above-mentioned alloy can be made detailed.

[0046] Furthermore, in the R2Fe14 B phase, it has the detailed diameter of average crystal grain comparable as a bcc-Fe phase originally. Moreover, since the space where the crystal grain of a bcc-Fe phase generates a large number in before R2Fe14 B phase deposits, and R2Fe14 B phase deposits is small It is not dependent on the programming rate in the temperature field to which R2Fe14 B phase deposits, and depends for the magnitude of the crystal grain of R2Fe14 B phase on the programming rate in the temperature field to which a first phase (bcc-Fe phase) deposits. That is, the diameter of average crystal grain of R2Fe14 B phase is made detailed by making a programming rate quick in the temperature field in which a first phase (bcc-Fe phase) deposits. Therefore, since the adjacent probability of the crystal grain of a bcc-Fe phase and the crystal grain of R2Fe14 B phase becomes high and the switched connection of a software magnetism phase (bcc(body-centered cubic structure)-Fe) and a hard magnetism phase (R2Fe14B) becomes is easy to be performed, a switched connection property improves, residual



magnetization ( $I_r$ ), a square shape ratio ( $I_r/I_s$ ), coercive force ( $iH_c$ ), and the maximum magnetic energy product ( $(BH)_{max}$ ) increase, and outstanding \*\*\*\*\* is obtained.

[0047] If it is in the hard magnetic material concerning this invention, Si element moreover, by Co being made to be contained in 0.5 – pentatomic % addition or T element in addition to Fe 0.5 to 50% in T element substitute The absolute value of the temperature coefficient of the magnetization when using it in the configuration from which a permeance coefficient becomes two or more The following [ 0.15% / K ], The absolute value of the temperature coefficient of the magnetization when using it in the configuration from which a permeance coefficient becomes ten or more especially can realize the following [ 0.1% / K ], and can raise the temperature characteristic. Therefore, the hard magnetic material concerning this invention can be used suitable for a magnetic type rotary encoder, a potentiometer and a sensor, an actuator, a loudspeaker, a motor, etc.

[0048]

[Example] (Example 1 of an experiment) The quenching thin band alloy of various presentations was heat-treated as follows, and the hard magnetic material was produced. First, the quenching thin band alloy with a thickness of about 20 micrometers was produced by producing an ingot with an arc solution process and blowing off the metal which dissolved on Cu roll which is rotating in Ar ambient atmosphere from the narrow width nozzle of 0.3mm of slit \*\*\*\*. Subsequently, the thin band alloy sample (example) heat-treated and obtained on the conditions which heat the obtained quenching thin band alloy by part for programming rate 180K/all over the infrared image furnace of  $1 \times 10^{-2}$  or less Pa, and are held for about 180 seconds by annealing temperature 1023K (750 degrees C) was obtained. Fe<sub>76</sub>Co<sub>10</sub>Nb<sub>2</sub>Pr<sub>7</sub>B<sub>5</sub> which each presentation of the thin band alloy sample obtained here has within the limits of this invention — the thin band alloy of a presentation, and Fe<sub>66</sub>Co<sub>20</sub>Nb<sub>2</sub>Pr<sub>7</sub>B<sub>5</sub> — the thin band alloy of a presentation, and Fe<sub>84</sub>Nb<sub>2</sub>Pr<sub>7</sub>B<sub>5</sub>Si<sub>2</sub> — it was the thin band alloy of a presentation.

[0049] the thin band alloy sample of the acquired example — VSM (oscillating sample mold magnetometer) — using — the inside of the impression magnetic field of 10kOe, and a vacuum — room temperature — about 490 — the demagnetization curve (the 2nd quadrant) in K was measured. A result is shown in drawing 5 – drawing 7. I is a straight line whose permeance coefficient ( $p$ ) is 10 (prism form) among drawing 5 – drawing 7, and RO is a straight line whose  $p$  is 1.5 (disc form). Moreover, the residual magnetization ( $I_r$ ) for which it asked from the demagnetization curve (the 2nd quadrant), and the temperature change of coercive force ( $iH_c$ ) are shown in drawing 8.

[0050] Moreover, the magnetic properties in the room temperature of the thin band alloy sample of an example are shown in a table 1. In addition,  $I_r/I_s$  is the rate (square shape ratio) of the residual magnetization ( $I_r$ ) to saturation magnetization ( $I_s$ ) among a table 1. Furthermore, the temperature coefficient of the residual magnetization in the room temperature of the thin band alloy sample of an example – about 490 K and coercive force and the temperature coefficient of the residual magnetization when considering as  $p = 1.5$  and the configuration used as  $p = 10$  are shown in a table 2.

[0051] The relation between the magnetic properties of the conventional ferrite magnet and a Nd-Fe-B system (Nd<sub>2</sub>Fe<sub>14</sub>B) magnet and temperature is shown in drawing 8 as an example of a comparison. Moreover, the residual magnetization of these conventional magnets and the temperature coefficient of coercive force are doubled and shown in a table 2.

[0052]

[A table 1]

磁気特性 (室温)

硬磁性材料の組成	$I_s(\text{emu g}^{-1})$	$I_r(\text{emu g}^{-1})$	$iH_c(\text{kOe})$	$I_r/I_s$
Fe <sub>76</sub> Co <sub>10</sub> Nb <sub>2</sub> Pr <sub>7</sub> B <sub>5</sub>	147.2	114.8	3.1	0.78
Fe <sub>66</sub> Co <sub>20</sub> Nb <sub>2</sub> Pr <sub>7</sub> B <sub>5</sub>	156.3	127.1	3.11	0.81
Fe <sub>84</sub> Nb <sub>2</sub> Pr <sub>7</sub> B <sub>5</sub> Si <sub>2</sub>	139.3	105.2	3.62	0.755

[0053]

[A table 2]

Ir及びiHcの温度係数 (室温～約490 K)

	硬磁性材料の組成	dIr/dT (%/K)	diHc/dT (%/K)	P=1.5のときの dI/dT(%/K)	P=10のときの dI/dT(%/K)
実施例	Fe <sub>88</sub> Nb <sub>2</sub> Pr <sub>5</sub> B <sub>5</sub>	-0.06	-0.43	-0.38	-0.12
	Fe <sub>76</sub> Co <sub>10</sub> Nb <sub>2</sub> Pr <sub>7</sub> B <sub>5</sub>	-0.02	-0.28	-0.20	-0.10
	Fe <sub>66</sub> Co <sub>20</sub> Nb <sub>2</sub> Pr <sub>7</sub> B <sub>5</sub>	-0.02	-0.36	-0.33	-0.08
	Fe <sub>84</sub> Nb <sub>2</sub> Pr <sub>7</sub> B <sub>5</sub> Si <sub>2</sub>	-0.02	-0.32	-0.17	-0.05
比較例	Fe <sub>77</sub> Nd <sub>15</sub> B <sub>8</sub>	-0.16	-0.4	--	--
	(Fe <sub>0.8</sub> Co <sub>0.1</sub> ) <sub>77</sub> Nd <sub>15</sub> B <sub>8</sub>	-0.11	-0.35	--	--
	フェライト磁石	-0.18	--	--	--

[0054] From drawing 8 and a table 2, as for the magnet of the thin band alloy sample of an example, and the example of a comparison, the inclination for residual magnetization (Ir) and coercive force (iHc) to decrease with lifting of temperature is accepted. the temperature coefficient (diHc/dT) of coercive force -- Fe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub> B<sub>5</sub> of an example -- the sample of a presentation is -0.43 %/K and is a value near the value (-0.4%/K) of the Nd-Fe-B system magnet of the example of a comparison. On the other hand, by the thin band alloy sample of the example which added Co and Si, being a value smaller than the magnet of Fe<sub>77</sub>Nd<sub>15</sub>B<sub>8</sub> of -0.28 -- -0.36% / K, and the example of a comparison is admitted. Thus, it is considered to originate in the Curie temperature of a hard magnetism phase rising by adding Co that the temperature coefficient of coercive force decreases.

[0055] next -- the temperature coefficient (dIr/dT) of residual magnetization -- Fe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub> B<sub>5</sub> of an example -- the samples of a presentation are -0.06%/K, and the value of the Nd-Fe-B system magnet (8 Fe<sub>77</sub>Nd<sub>15</sub>B<sub>8</sub> 77 (Fe<sub>0.9</sub>Co<sub>0.1</sub>) Nd<sub>15</sub>B<sub>8</sub> magnet of a presentation) of the example of a comparison is low compared with being -0.11 -- -0.16%/K. the phase to which this participates in magnetization with the magnet of the example of a comparison -- a hard magnetism phase -- it is -- it receives and it is thought by the thin band alloy sample of an example that it is because it has the nano diplophase organization where the hard magnetism phase and the soft magnetism phase with the small rate of a temperature change of magnetization (bcc-Fe phase) were intermingled. Moreover, by the thin band alloy sample of the example which added Co and Si, it is admitted that the temperature coefficients of Ir are -0.02% / K, and a substantially small value. drawing 6 to Fe<sub>66</sub>Co<sub>20</sub>Nb<sub>2</sub>Pr<sub>7</sub> B<sub>5</sub> -- especially in the sample of a presentation, the temperature change of magnetization is small in ten or more [ p = ] fields, and it turns out that the temperature characteristic is excellent.

[0056] It asks for drawing 9 from the demagnetization curve which shows the value of the residual magnetization (Ir) in each temperature when using the thin band alloy sample of an example in p= 1.5 and the configuration used as p= 10, respectively to drawing 5 - drawing 7 . Moreover, the temperature change of the residual magnetization (Ir) when using a conventional Sm-Co magnet and a conventional Nd-Fe-B system magnet (Nd<sub>2</sub>Fe<sub>14</sub>B presentation) for drawing 9 in p= 1.5 and the configuration used as p= 10 as a comparison, respectively is doubled and shown. Fe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub> B<sub>5</sub> which drawing 10 has within the limits of the presentation of this invention -- the sintering bulk (alloy consolidation object) sample of a presentation, and Fe<sub>86</sub>Nb<sub>2</sub>Pr<sub>7</sub> B<sub>5</sub> -- the relation between the permeance coefficient of the thin band alloy sample of a presentation and the temperature coefficient of residual magnetization is shown. Moreover, the relation between the permeance coefficient of the conventional Nd-Fe-B system magnet (Nd<sub>2</sub>Fe<sub>14</sub>B presentation) and a temperature coefficient is doubled and shown in drawing 10 as a comparison.

[0057] In the case of p= 1.5 and a low permeance coefficient, from a table 2 and drawing 8 - drawing 10 Fe<sub>84</sub>Nb<sub>2</sub>Pr<sub>7</sub> B<sub>5</sub>Si<sub>2</sub> which is the example which added Si -- Fe<sub>76</sub>Co<sub>10</sub>Nb<sub>2</sub>Pr<sub>7</sub> B<sub>5</sub> which the temperature

coefficients of magnetization of the sample of a presentation are  $-0.17\%/K$ , and is the example which added Co -- with a presentation Fe66Co20Nb2Pr7 B5 -- the temperature coefficient of magnetization of the sample of a presentation respectively  $-0.20\%/K$ , and  $-0.33\%/K$  -- it is -- moreover, Fe88Nb2Pr5 B5 -- as for the temperature coefficient of magnetization of the sample of a presentation,  $-0.38\%/K$ , and each example have the comparatively high temperature coefficient equivalent to the conventional material. however -- the time of using it by  $p=10$  and the high permeance coefficient -- Fe88Nb2Nd5 B5 of an example -- the temperature coefficient of magnetization is  $-0.12\%/K$ , and the sample of a presentation is the same degree as the temperature coefficient of magnetization of the conventional Nd-Fe-B system magnet. Fe84Nb2Pr7 B5Si2 of the example which added Si on the other hand -- Fe66Co20Nb2Pr7 B5 of the example which the samples of a presentation are  $-0.05\%/K$ , and added Co -- the sample of a presentation indicates it to be  $-0.08\%/K$  that change of the magnetic properties by temperature is still smaller. moreover, when it is used in the configuration used as  $p=10$  the thin band alloy sample of an example -- especially -- Fe66Co20Nb2Pr7 B5 -- the sample of a presentation In the operating temperature range of 300 – 430K (27–157 degrees C) degree, the absolute value of the temperature coefficient of magnetization is small, it has the temperature characteristic which was excellent in the same degree as the Sm-Co system magnet of the example of a comparison, and it turns out that the temperature characteristic is superior to the Nd2Fe14B system magnet of the example of a comparison. [0058] From a table 2 and drawing 8 – drawing 10 , the sample of an example When it is the same degree as the absolute value of the temperature coefficient of magnetization of the Nd2Fe14B system magnet of the example of a comparison, or is small, when the permeance coefficient used it or more by two, and a permeance coefficient uses it or more by ten especially, The value smaller than  $0.1\%/K$  is acquired, the temperature coefficient of magnetization has the absolute value of the temperature coefficient of magnetization smaller than the Nd-Fe-B system magnet of the example of a comparison, and it turns out that the temperature characteristic is excellent.

[0059] (Example 2 of an experiment) the example 1 of an experiment -- the same -- carrying out -- Fe90Nb2Nd five B3, Fe89Nb2Nd5 B4, Fe89Nb2Nd4 B5, and Fe79Co10Nb2Nd4 B5 -- the thin band alloy sample of a presentation was obtained. the obtained thin band alloy sample -- VSM (oscillating sample mold magnetometer) -- using -- the inside of the impression magnetic field of 10kOe, and a vacuum -- room temperature -- the demagnetization curve (the 2nd quadrant) in about 160 degrees C was measured, and it asked for the temperature coefficient of coercive force. A result is shown in a table 3. Moreover, the temperature coefficient of the coercive force in room temperature  $-200$  degree C of conventional Fe77Nd15B8 and the thin band alloy sample of the presentation which becomes 77(Fe0.9Co0.1) Nd15B8 is doubled and shown in a table 3. Furthermore, the relation of the temperature and coercive force ( $iH_c$ ) which were acquired from the demagnetization curve is shown in drawing 11 .

[0060]

[A table 3]

硬磁性材料の組成	温度範囲	$diH_c/dT$ (%/K)
Fe <sub>88</sub> Nb <sub>2</sub> Nd <sub>5</sub> B <sub>5</sub>	室温～44℃	-0.22
	室温～66℃	-0.22
	室温～86℃	-0.25
	室温～105℃	-0.26
	室温～125℃	-0.27
Fe <sub>88</sub> Nb <sub>2</sub> Nd <sub>5</sub> B <sub>5</sub>	室温～55℃	-0.08
	室温～76℃	-0.09
	室温～94℃	-0.17
	室温～115℃	-0.19
	室温～135℃	-0.21
Fe <sub>88</sub> Nb <sub>2</sub> Nd <sub>5</sub> B <sub>5</sub>	室温～44℃	-0.33
	室温～65℃	-0.31
	室温～86℃	-0.26
	室温～105℃	-0.30
	室温～125℃	-0.31
	室温～146℃	-0.32
Fe <sub>77</sub> Co <sub>10</sub> Nb <sub>2</sub> Nd <sub>5</sub> B <sub>8</sub>	室温～56℃	-0.31
	室温～77℃	-0.28
	室温～97℃	-0.29
	室温～115℃	-0.30
	室温～137℃	-0.30
	室温～158℃	-0.29
Fe <sub>77</sub> Nd <sub>15</sub> B <sub>8</sub>	室温～200℃	-0.40
(Fe <sub>88</sub> Co <sub>10</sub> ) <sub>77</sub> Nd <sub>15</sub> B <sub>8</sub>	室温～200℃	-0.35

[0061] It turns out that each absolute value of the temperature coefficient of coercive force is low rather than 0.35% / K, and the thin band alloy sample of this example has the small temperature change of coercive force so that clearly [ in a table 3 ]. It turns out that the absolute value of the temperature coefficient of a room temperature - 100 degrees C [ of abbreviation ] coercive force becomes below 0.30% / K, and it excels in the temperature characteristic especially. On the other hand, about conventional Fe77Nd 15B8 and the thin band alloy sample of the presentation which becomes 77(Fe0.9Co0.1) Nd15B8, the absolute values of the temperature coefficient of coercive force are 0.4%/K, and 0.35%/K, respectively, and are larger than the thin band alloy sample of this example. Moreover, coercive force (iHc) is declining gently with lifting of temperature so that clearly from drawing 11 . Therefore, when such a thin band alloy sample (permanent magnet) is used for a magnetometric sensor, even if the operating temperature of a magnetometric sensor rises rapidly, since change of coercive force (iHc) is small, the drift of the output from a magnetometric sensor can be made small.

[0062] (Example 3 of an experiment) the example 1 of an experiment — the same — carrying out — Fe88Nb2Nd5 B5 — the quenching thin band alloy of a presentation was produced. Subsequently, the thin band alloy sample was obtained by carrying out temperature up of the obtained quenching thin band alloy to 750 degrees C all over the infrared image furnace of 1x10 - 2 or less Pa, and heat-treating on the conditions held for about 180 seconds. About the programming rate of heat treatment, as shown in drawing 12 , the thin band alloy sample heat-treated with various programming rates was obtained by considering as a part for 3K/ from a room temperature (27 degrees C) to T1 to a part for 180K/, and T1 to 750 degrees C (1023K), and changing T1 into arbitration for every sample in 27-750 degrees C. Furthermore, as shown in drawing 13 , it considers as a part for 180K/ from a room temperature (27 degrees C) to T2 to a part for 3K/, and T2 to 750 degrees C, and T2 is changed into arbitration for every sample in 27-750 degrees C. By carrying out, the thin band alloy sample heat-treated with various programming rates was obtained.

[0063] About the quenching thin band alloy, the programming rate was considered as a part for 6 – 40K/, and DSC measurement (differential scanning calorimetry) was performed. A result is shown in drawing 14 . Also in which programming rate, the exothermic peak by crystallization of a bcc-Fe phase is checked in the range of 500–650 degrees C. Moreover, in a temperature requirement 650 degrees C or more, the exothermic peak by crystallization of Nd<sub>2</sub>Fe<sub>14</sub> B phase is checked.

[0064] The result of having investigated the dependency of T<sub>1</sub> of the residual magnetization (I<sub>r</sub>) of the thin band alloy sample which T<sub>1</sub> was changed to arbitration in 27–750 degrees C, and was obtained, a remanence ratio (I<sub>r</sub>/I<sub>s</sub>), and coercive force (iH<sub>c</sub>) is shown in drawing 15 . As for I<sub>r</sub>, I<sub>r</sub>/I<sub>s</sub>, and iH<sub>c</sub>, T<sub>1</sub> is low below 500 degrees C, and it turns out that \*\*\*\*\* has deteriorated so that clearly from drawing 15 . T<sub>1</sub> this from drawing 12 below 500 degrees C Since the minimum of the temperature requirement for programming rate 3K/becomes 500 degrees C or less and a programming rate becomes low in the temperature requirement (500–650 degrees C) where a bcc-Fe phase deposits The number of generating nucleus sites of a bcc-Fe phase decreases, the diameter of crystal grain of the Nd<sub>2</sub>Fe<sub>14</sub> B phase which deposits and grows from between the grains of a bcc-Fe phase and a bcc-Fe phase as a result becomes large, and that in which switched connection nature fell to and \*\*\*\*\* deteriorated is presumed. Moreover, in the case (T<sub>1</sub> is 650 degrees C) where the temperature requirement for programming rate 3K/is 650–750 degrees C, the programming rate is low in the temperature requirement where Nd<sub>2</sub>Fe<sub>14</sub> B phase deposits. Although we were anxious about lowering of the switched connection nature by hypertrophy of the crystal grain of Nd<sub>2</sub>Fe<sub>14</sub> B phase, the \*\*\*\*\* of the obtained thin band alloy sample was good actually, as shown in drawing 15 . Since the space where many crystal grain of a bcc-Fe phase already deposits under a quick programming rate, and Nd<sub>2</sub>Fe<sub>14</sub> B phase deposits was small relatively, the grain growth in the case of the deposit of Nd<sub>2</sub>Fe<sub>14</sub> B phase was controlled, and switched connection nature improved, this is presumed.

[0065] Next, the result of having investigated the dependency of T<sub>2</sub> of the residual magnetization (I<sub>r</sub>) of the thin band alloy sample which T<sub>2</sub> was changed to arbitration in 27–750 degrees C, and was obtained, a remanence ratio (I<sub>r</sub>/I<sub>s</sub>), and coercive force (iH<sub>c</sub>) is shown in drawing 16 . T<sub>2</sub> is residual magnetization (I<sub>r</sub>) and a square shape above 650 degrees C so that clearly from drawing 16 . A ratio (I<sub>r</sub>/I<sub>s</sub>) and coercive force (iH<sub>c</sub>) are low, and it turns out that \*\*\*\*\* has deteriorated. For this, drawing 13 to T<sub>2</sub> is a temperature requirement for programming rate 3K/above 650 degrees C. Since a maximum becomes 650 degrees C or more and the programming rate in the temperature requirement (500–650 degrees C) where a bcc-Fe phase deposits becomes low, the crystal grain of a bcc-Fe phase \*\*\*\*\* , and that in which switched connection nature with Nd<sub>2</sub>Fe<sub>14</sub> B phase fell to, and \*\*\*\*\* deteriorated is presumed.

[0066] By considering a programming rate as the above by 10K/from the above result into the temperature requirement where a presentation is the range of this invention, and a bcc-Fe phase (first phase) deposits (500–650 degrees C) shows that the thin band alloy sample excellent in \*\*\*\*\* is obtained.

[0067] (Example 4 of an experiment) Fe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub> B5 -- the temperature change of magnetization of the hard magnetic material which heat-treated the amorphous alloy thin band after quenching of a presentation with the annealing temperature of 750 degrees C, and was obtained was investigated. moreover, Fe<sub>88</sub>Pr<sub>7</sub> B5 -- the temperature change of magnetization of the hard magnetic material which heat-treated the amorphous alloy thin band after quenching of a presentation with the annealing temperature of 650 degrees C, and was obtained was investigated. The result is shown in drawing 17 . drawing 17 -- Fe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub> B5 -- the hard magnetic material of a presentation, and Fe<sub>88</sub>Pr<sub>7</sub> B5 -- the temperature change of magnetization of the hard magnetic material of a presentation is shown. Magnetization is decreasing at two steps with lifting of temperature as shown in drawing 17 . It is admitted that two phases of phases which participate in magnetization of a hard magnetic material exist from this. Moreover, since the degree of reduction in magnetization is changing near 315 degree C, this neighborhood is the Curie temperature of a Fe<sub>14</sub>Nd<sub>2</sub>B phase, and since the degree of reduction in magnetization is changing near 770 degree C, it turns out that this neighborhood is the Curie temperature of a bcc-Fe phase. In addition, it is considered to be because for a volume fraction to be [ that magnetization is low and ] small that the step of the magnetization which originates in an amorphous phase here is not seen.

[0068] moreover, Fe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub> B5 obtained here — the hard magnetic material of a presentation, and Fe<sub>88</sub>Pr<sub>7</sub> B5 — the 2nd quadrant of the magnetization curve of the hard magnetic material of a presentation is shown in drawing 18 . The magnetization curve is the same magnetization curve as the magnetic material which consists of a single phase as which a step is not regarded, and it is clear that the switched connection magnet which the detailed software magnetism phase and the hard magnetism phase combined magnetically is obtained as shown in drawing 18 .

[0069]

[Effect of the Invention] As explained above, the hard magnetic material of this invention The element R which consists or more of one of one or more sorts of Elements T and rare earth elements of Fe, Co, and the nickel Since the absolute values of the temperature coefficient of the magnetization when using it in the configuration from which it consists of an alloy containing B, and a permeance coefficient becomes two or more are below 0.15% / K and coercive force (iH<sub>c</sub>) is the thing of 1 or more kOes Since the drift of the output resulting from a temperature change can be prevented when the temperature characteristic is excellent and it uses for a sensor etc., the reliability of detection precision can be raised. Moreover, the diameter of average crystal grain of the bcc-Fe phase of a fine crystalline phase which deposited by heat treatment has made this hard magnetic material detailed, the switched connection property of a software magnetism phase (bcc(body-centered cubic structure)-Fe) and a hard magnetism phase (R<sub>2</sub>Fe<sub>14</sub>B) is improving, and outstanding \*\*\*\*\* is obtained. Furthermore, since good \*\*\*\*\* is obtained even if it lessens the content of rare earth elements R, this hard magnetic material can be manufactured with a comparatively low manufacturing cost.

[0070] The hard magnetic material of this invention Moreover, the software magnetism phase or semi- hard magnetism phase of 1 or less kOe of coercive force, It consists of an alloy which contains the hard magnetism phase of 1 or more kOes of coercive force more than 10vol(s)(volume) %, respectively. Since the absolute values of the temperature coefficient of the magnetization when using it in the configuration from which a permeance coefficient becomes two or more are below 0.15% / K and coercive force is the thing of 1 or more kOes There is an advantage that can have each property of a software magnetism phase and a hard magnetism phase, and \*\*\*\*\* is excellent in low cost, and moreover the temperature characteristic is excellent. Moreover, the hard magnetic material of this invention consists of an alloy with which the magnetic phase and Curie temperature of 600 degrees C or more contain [ Curie temperature ] the magnetic phase of 600 degrees C or less more than 10vol(s)(volume) %, respectively. Since the absolute values of the temperature coefficient of the magnetization when using it in the configuration from which a permeance coefficient becomes two or more are below 0.15% / K and coercive force is the thing of 1 or more kOes There is an advantage that can have each property of a software magnetism phase and a hard magnetism phase, and \*\*\*\*\* is excellent in low cost, and moreover the temperature characteristic is excellent.

[0071] The hard magnetic material of this invention among Fe, Co, and nickel One or more sorts of elements T Since it consists of an alloy containing the elements R and B which consist of one or more sorts in rare earth elements, the absolute values of the temperature coefficient of coercive force are below 0.35% / K and coercive force is the thing of 1 or more kOes When it is especially used for a small sensor etc., a magnet becomes two or less configuration by the permeance coefficient. Magnetic \*\*\*\*\* will be influenced by the temperature coefficient of coercive force, and since it can prevent the drift of the output resulting from the temperature change of a small sensor etc., it can raise the reliability of detection precision.

[0072] Moreover, the hard magnetic material of this invention consists of an alloy which contains the software magnetism phase of 1 or less kOe of coercive force, and the hard magnetism phase of 1 or more kOes of coercive force more than 10vol(s)(volume) %, respectively. Since the absolute values of the temperature coefficient of coercive force are below 0.35% / K and coercive force is the thing of 1 or more kOes, there is an advantage that can have the middle property of a software magnetism phase and a hard magnetism phase, and \*\*\*\*\* is excellent in low cost, and moreover the temperature characteristic is excellent. Moreover, the hard magnetic material of this invention consists of an alloy with which the

magnetic phase and Curie temperature of 600 degrees C or more contain [ Curie temperature ] the magnetic phase of 600 degrees C or less more than 10vol(s)(volume) %, respectively. Since the absolute values of the temperature coefficient of coercive force are below 0.35% / K and coercive force is the thing of 1 or more kOes, there is an advantage that can have the middle property of a soft magnetism phase and a hard magnetism phase, and \*\*\*\*\* is excellent in low cost, and moreover the temperature characteristic is excellent.

[0073] In the hard magnetic material concerning this invention, if it is in some which contain the fine crystalline phase of 100nm or less of diameters of average crystal grain as a subject, especially, the switched connection property of a soft magnetism phase and a hard magnetism phase can be excellent, and \*\*\*\*\* can be raised more. Moreover, if it is in some by which the alloy which makes the main phase the amorphous phase which quenched the alloy molten metal and was obtained in the hard magnetic material concerning this invention was heat-treated, it is low cost and the hard magnetic material in which \*\*\*\*\* is excellent in and the temperature characteristic is moreover excellent is obtained suitably.

[0074] The alloy which makes the main phase the amorphous phase which quenched the alloy molten metal of the above-mentioned configuration, and was especially obtained in the hard magnetic material concerning this invention If it is in the thing which it comes to heat-treat with the above programming rate by 10K/in the temperature requirement where the first phase of a crystalline substance phase deposits at least While much crystal grain of a bcc-Fe phase can form and being able to prevent hypertrophy of the crystal grain Since hypertrophy of the crystal grain of the R2Fe14 B phase generated later can also be prevented, the diameter of average crystal grain of the bcc-Fe phase of a fine crystalline phase and R2Fe14 B phase which deposits in the above-mentioned alloy can be made detailed. Moreover, in R2Fe14 B phase, although the programming rate dependency of particle size is larger than the case of a bcc-Fe phase Since the space where the crystal grain of a bcc-Fe phase generates a large number in before R2Fe14 B phase deposits, and R2Fe14 B phase deposits is small The magnitude of the crystal grain of R2Fe14 B phase is not based on the programming rate in the temperature requirement where R2Fe14 B phase deposits, but it depends for it on the programming rate in the temperature requirement where a first phase (bcc-Fe phase) deposits. That is, the diameter of crystal grain of R2Fe14 B phase is made detailed by carrying out high-speed temperature up in the temperature field in which a first phase deposits. The adjacent probability of the crystal grain of a bcc-Fe phase and the crystal grain of R2Fe14 B phase becomes high, by that, since the switched connection of a soft magnetism phase (bcc(body-centered cubic structure)-Fe) and a hard magnetism phase (R2Fe14B) becomes is easy to be performed, a switched connection property improves, and outstanding \*\*\*\*\* is obtained.

[0075] In the hard magnetic material concerning this invention, if the absolute value of the temperature coefficient of the magnetization when using it in the configuration from which a permeance coefficient becomes two or more is one of those which were made into below 0.10% / K, the temperature characteristic is excellent especially. Moreover, in the hard magnetic material concerning this invention, if the absolute value of the temperature coefficient of the magnetization when using it in the configuration from which a permeance coefficient becomes ten or more is one of those which were made into below 0.08% / K, the temperature characteristic is excellent especially. Furthermore, in the hard magnetic material concerning this invention, if it is in some which the absolute value of the temperature coefficient of room temperature -100 degree C coercive force made below 0.30% / K, the temperature characteristic is excellent especially.

[0076] According to the hard magnetic material concerning this invention, coercive force can realize the hard magnetic material of 2 or more kOes. Moreover, according to the hard magnetic material concerning this invention, 0.6 or more hard magnetic materials can be realized comparatively ( $I_r/I_s$ ), therefore high residual magnetization ( $I_r$ ) can be realized, and the hard magnetic material with the high maximum magnetic energy product ((BH) max) of the residual magnetization ( $I_r$ ) to saturation magnetization ( $I_s$ ) can be obtained. If it is in the hard magnetic material of this invention, x which sets a presentation to  $T_xMyR_zB_w$  and shows a presentation ratio, and y, z and w are atomic %s.  $50 \leq x$ ,  $0 \leq y \leq 15$ ,  $3 \leq z \leq 20$ , and the relation

it is unrelated  $2 \leq w \leq 20$  are satisfied. By satisfying preferably  $80 \leq x \leq 93$ ,  $1 \leq y \leq 5$ ,  $3 \leq z \leq 10$ , and the relation it is unrelated  $3 \leq w \leq 7$ , and satisfying more preferably  $86 \leq x \leq 93$ ,  $1 \leq y \leq 3$ ,  $3 \leq z \leq 7$ , and the relation it is unrelated  $3 \leq w \leq 5$ . And since the compound which a good amorphous phase is obtained and gives \*\*\*\*\* from the thing [ that stress relief heat treatment is carried out ] deposits even if the concentration of rare earth elements is low, when residual magnetization (Ir) considers as the thing of 100 or more emu/g It has \*\*\*\*\* excellent in low cost, and the hard magnetic material excellent in the temperature characteristic is obtained.

[0077] If it is in the hard magnetic material of this invention, it can also have corrosion resistance further by setting a presentation to  $T_xM_yR_zB_wE_v$ , and x which shows a presentation ratio, and y, z, w and v being atomic %, and satisfying  $50 \leq x$ ,  $0 \leq y \leq 15$ ,  $3 \leq z \leq 20$ ,  $2 \leq w \leq 20$ , and the relation it is unrelated  $0 \leq v \leq 10$ . x which shows the presentation ratio in an empirical formula here, and y, z, w and v moreover, by atomic %. In also having corrosion resistance  $80 \leq x \leq 93$ ,  $1 \leq y \leq 5$ ,  $3 \leq z \leq 10$ ,  $3 \leq w \leq 7$ ,  $0 \leq v \leq 5$ , and by satisfying more preferably  $86 \leq x \leq 93$ ,  $1 \leq y \leq 3$ ,  $3 \leq z \leq 7$ ,  $3 \leq w \leq 5$ , and the relation it is unrelated  $0.1 \leq v \leq 5$ , more excellent \*\*\*\*\* can be obtained. In the hard magnetic material concerning this invention, the temperature characteristic can be raised more that 0.5- pentatomic % addition of Si element is done in T element substitute, or by containing Co in T element in addition to Fe. Therefore, if it is in the hard magnetic material of this invention, it is useful as a magnet material used for various kinds of equipments, such as a magnetic type rotary encoder, a potentiometer and a sensor, an actuator, a loudspeaker, and a motor, and reduction of a manufacturing cost can be aimed at.

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[Translation done.]



**\* NOTICES \***

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1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] It is the perspective diagram showing the example of the operation gestalt which applied the hard magnetic material of this invention to the magnet for hole potentiometers.

[Drawing 2] It is the perspective diagram showing the example of the operation gestalt which applied the hard magnetic material of this invention to the magnet for magnetic type rotary encoders.

[Drawing 3] It is the cross section showing the first example of the operation gestalt which applied the hard magnetic material of this invention to the magnet for loudspeakers.

[Drawing 4] It is the cross section showing the second example of the operation gestalt which applied the hard magnetic material of this invention to the magnet for loudspeakers.

[Drawing 5] Fe<sub>76</sub>Co<sub>10</sub>Nb<sub>2</sub>Pr<sub>7</sub> B<sub>5</sub> — it is the graph which shows the demagnetization curve (the 2nd quadrant) in 302.5K–489K of the thin band alloy sample of a presentation.

[Drawing 6] Fe<sub>66</sub>Co<sub>20</sub>Nb<sub>2</sub>Pr<sub>7</sub> B<sub>5</sub> — it is the graph which shows the demagnetization curve (the 2nd quadrant) in 308K–471K of the thin band alloy sample of a presentation.

[Drawing 7] It is the graph which shows the demagnetization curve (the 2nd quadrant) in 301.5K–477K of the thin band alloy sample of the becoming presentation Fe<sub>84</sub>Nb<sub>2</sub>Pr<sub>7</sub> B<sub>5</sub>Si<sub>2</sub>.

[Drawing 8] It is drawing showing the relation between the magnetic properties of the magnet of the thin band alloy sample of an example, and the example of a comparison, and temperature.

[Drawing 9] It is drawing showing the temperature change of Ir when using the magnet of the thin band alloy sample of an example, and the example of a comparison in the configuration set to p= 1.5 and p= 10, respectively.

[Drawing 10] It is drawing showing the relation between the permeance coefficient of the sintering bulk (alloy consolidation object) which is within the limits of the presentation of this invention, the thin band alloy which is within the limits of the presentation of this invention, and the conventional Nd-Fe-B system magnet, and a temperature coefficient.

[Drawing 11] It is the graph which shows the relation of the temperature (T) of a thin band alloy and coercive force (iH<sub>c</sub>) which are within the limits of the presentation of this invention.

[Drawing 12] It is drawing for explaining the pattern of a programming rate.

[Drawing 13] It is drawing for explaining the pattern of a programming rate.

[Drawing 14] Fe<sub>88</sub>Nb<sub>2</sub>Nd<sub>5</sub> B<sub>5</sub> obtained by the quenching method — amorphous \*\* of a presentation It is drawing showing the DSC (differential scanning calorimetry) curve in each programming rate of a \*\*\*\*\* sample.

[Drawing 15] Fe<sub>88</sub>Nb<sub>2</sub>Nd<sub>5</sub> B<sub>5</sub> — it is the graph which shows the dependency of T<sub>1</sub> of Ir of the sample of a presentation, Ir/I<sub>s</sub>, and i H<sub>c</sub>.

[Drawing 16] Fe<sub>88</sub>Nb<sub>2</sub>Nd<sub>5</sub> B<sub>5</sub> — it is the graph which shows the dependency of T<sub>2</sub> of Ir of the sample of a presentation, Ir/I<sub>s</sub>, and i H<sub>c</sub>.

[Drawing 17] Fe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub> B<sub>5</sub> — the hard magnetic material of a presentation, and Fe<sub>88</sub>Pr<sub>7</sub> B<sub>5</sub> — it is the graph which shows the temperature change of magnetization of the hard magnetic material of a presentation.

[Drawing 18] Fe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub> B<sub>5</sub> — the hard magnetic material of a presentation, and Fe<sub>88</sub>Pr<sub>7</sub> B<sub>5</sub> — it is the graph which shows the 2nd quadrant of the magnetization curve of the hard magnetic material of a

presentation.

[Description of Notations]

1 [ ... The disc section, 5 / ... Inlet connection, 10 / ... The magnet for rotary encoders, 21 / ... Pole piece, 22 / ... \*\* / 23 A powder core (yoke) 24 / ... Pole piece, 33 / ... A magnet, 34 / ... A yoke, 35 ... A cone-like diaphragm, 36 / ... Magnetic-shielding covering, 37 / ... bolt, 38 / ... washer, 39 ... Nut. / ... A magnet, 25 ... 31 A cone-like diaphragm, 32 ] ... The magnet section, 2 ... A supporter, 3 ... The notching section, 4

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最終頁に続く

(54) 【発明の名称】 硬磁性材料

(57) 【要約】

【課題】 低コストで、硬磁気特性が優れ、しかも温度特性が優れた硬磁性材料を提供する。

【解決手段】 Fe、Co、Niのうちの1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含む合金からなり、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下であり、保磁力が1kOe以上であり、更に保磁力の温度係数の絶対値が0.35%/K以下であることを特徴とする硬磁性材料を採用する。

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## 【特許請求の範囲】

【請求項1】 Fe、Co、Niのうちの1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bを含む合金からなり、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下であり、保磁力が1kOe以上であることを特徴とする硬磁性材料。

【請求項2】 保磁力1kOe以下のソフト磁性相または準ハード磁性相と保磁力1kOe以上のハード磁性相とをそれぞれ10vol(体積)%以上含む合金からなり、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下であり、保磁力が1kOe以上であることを特徴とする硬磁性材料。

【請求項3】 キュリー温度が600℃以上の磁性相とキュリー温度が600℃以下の磁性相とをそれぞれ10vol(体積)%以上含む合金からなり、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下であり、保磁力が1kOe以上であることを特徴とする硬磁性材料。

【請求項4】 Fe、Co、Niのうちの1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bを含む合金からなり、保磁力の温度係数の絶対値が0.35%/K以下であり、保磁力が1kOe以上であることを特徴とする硬磁性材料。

【請求項5】 保磁力1kOe以下のソフト磁性相と保磁力1kOe以上のハード磁性相とをそれぞれ10vol(体積)%以上含む合金からなり、保磁力の温度係数の絶対値が0.35%/K以下であり、保磁力が1kOe以上であることを特徴とする硬磁性材料。

【請求項6】 キュリー温度が600℃以上の磁性相とキュリー温度が600℃以下の磁性相とをそれぞれ10vol(体積)%以上含む合金からなり、保磁力の温度係数の絶対値が0.35%/K以下であり、保磁力が1kOe以上であることを特徴とする硬磁性材料。

【請求項7】 平均結晶粒径100nm以下の微細結晶質相を主相として含むことを特徴とする請求項1～6のいずれかに記載の硬磁性材料。

【請求項8】 合金溶湯を急冷して得られた非晶質相を主相とする合金が熱処理されてなるものであることを特徴とする請求項1～7のいずれかに記載の硬磁性材料。

【請求項9】 合金溶湯を急冷して得られた非晶質相を主相とする合金が、少なくとも結晶質相の初相が析出する温度範囲において10K/分以上の昇温速度で熱処理されてなるものであることを特徴とする請求項1～8のいずれかに記載の硬磁性材料。

【請求項10】 パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.10%/K以下のものであることを特徴とする請求項1～9のいずれかに記載の硬磁性材料。

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【請求項11】 パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が0.08%/K以下のものであることを特徴とする請求項1～10のいずれかに記載の硬磁性材料。

【請求項12】 室温から100℃の温度範囲での保磁力の温度係数の絶対値が0.30%/K以下であることを特徴とする請求項1～11のいずれかに記載の硬磁性材料。

【請求項13】 保磁力が2kOe以上のものであることを特徴とする請求項1～12のいずれかに記載の硬磁性材料。

【請求項14】 飽和磁化(I<sub>s</sub>)に対する残留磁化(I<sub>r</sub>)の割合(I<sub>r</sub>/I<sub>s</sub>)が、0.6以上のものであることを特徴とする請求項1～13のいずれかに記載の硬磁性材料。

【請求項15】 下記の組成式で表され、残留磁化(I<sub>r</sub>)が100emu/g以上のものであることを特徴とする請求項1～14のいずれかに記載の硬磁性材料。

$T_xM_yR_zB_w$

ただし、TはFe、Co、Niのうち1種以上の元素を表わし、MはZr、Nb、Ta、Hf、Ti、V、Mo、Wのうち1種以上の元素を表わし、Rは希土類元素のうち1種以上の元素を表わすとともに、組成比を示すx、y、z、wは原子%で、 $50 \leq x$ 、 $0 \leq y \leq 15$ 、 $3 \leq z \leq 20$ 、 $2 \leq w \leq 20$ である。

【請求項16】 前記組成式中の組成比を示すx、y、z、wは原子%で、 $80 \leq x \leq 93$ 、 $1 \leq y \leq 5$ 、 $3 \leq z \leq 10$ 、 $3 \leq w \leq 7$ であることを特徴とする請求項15に記載の硬磁性材料。

【請求項17】 前記組成式中の組成比を示すx、y、z、wは原子%で、 $86 \leq x \leq 93$ 、 $1 \leq y \leq 3$ 、 $3 \leq z \leq 7$ 、 $3 \leq w \leq 5$ であることを特徴とする請求項15に記載の硬磁性材料。

【請求項18】 前記組成式中の組成比を示すx、y、z、wは原子%で、 $x = 100 - y - z - w$ 、 $1 \leq y \leq 3$ 、 $3 \leq z \leq 7$ 、 $3 \leq w \leq 5$ であることを特徴とする請求項15に記載の硬磁性材料。

【請求項19】 下記の組成式で表されることを特徴とする請求項1～14のいずれかに記載の硬磁性材料。

$T_xM_yR_zB_wE_v$

ただし、TはFe、Co、Niのうち1種以上の元素を表わし、MはZr、Nb、Ta、Hf、Ti、V、Mo、Wのうち1種以上の元素を表わし、Rは希土類元素のうち1種以上の元素を表わし、EはCr、Al、Pt、Ru、Rh、Pd、Os、Ir、Cu、Ag、Au、Ga、Geのうち1種以上の元素を表わすとともに、組成比を示すx、y、z、w、vは原子%で、 $50 \leq x$ 、 $0 \leq y \leq 15$ 、 $3 \leq z \leq 20$ 、 $2 \leq w \leq 20$ 、 $0 \leq v \leq 10$ である。

【請求項20】 前記組成式中の組成比を示すx、y、

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z、w、vは原子%で、 $80 \leq x \leq 93$ 、 $1 \leq y \leq 5$ 、 $3 \leq z \leq 10$ 、 $3 \leq w \leq 7$ 、 $0 \leq v \leq 5$ であることを特徴とする請求項19に記載の硬磁性材料。

【請求項21】 前記組成式中の組成比を示すx、y、z、w、vは原子%で、 $x = 100 - y - z - w - v$ 、 $1 \leq y \leq 3$ 、 $3 \leq z \leq 7$ 、 $3 \leq w \leq 5$ 、 $0.1 \leq v \leq 5$ であることを特徴とする請求項19に記載の硬磁性材料。

【請求項22】 前記組成式中の組成比を示すx、y、z、w、vは原子%で、 $86 \leq x \leq 93$ 、 $1 \leq y \leq 3$ 、 $3 \leq z \leq 7$ 、 $3 \leq w \leq 5$ 、 $0.1 \leq v \leq 5$ であることを特徴とする請求項19に記載の硬磁性材料。

【請求項23】 請求項1～22のいずれかに記載の硬磁性材料において、SiがT元素置換で0.5～5原子%添加されてなることを特徴とする硬磁性材料。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、磁気式エンコーダ、ポテンシオメータ、センサ、モータ、アクチュエータ、スピーカなどに使用できる磁気性能に優れ、しかも温度特性が優れた硬磁性材料に関する。

【0002】

【従来の技術】一般に、フェライト磁石やアルニコ磁石(A1-Ni-Co-Fe系磁石)よりも優れた性能を有する硬磁性材料としては、Sm-Co系磁石、Nd-Fe-B系磁石などが知られており、またさらに高い性能を目指してSm-Fe-N系磁石などの新しい合金磁石の研究も数多くなされている。

【0003】

【発明が解決しようとする課題】しかし、これらの硬磁性材料は、10原子%以上のNd、または8原子%以上のSmを含み、高価な希土類元素の使用量が多いためにフェライト磁石やアルニコ磁石よりも製造コストが高くなってしまうという課題があった。また、Nd-Fe-B系磁石は、温度による磁気特性の変化が大きいためにセンサの構成材料としては使用できないという課題があった。また、Sm-Co系磁石は、磁化の温度係数の絶対値が小さい磁石であるが、Nd-Fe-B系磁石よりも高価な磁石であるため、使用できる範囲が限られていた。一方、フェライト磁石は、上述のように希土類元素を含む磁石に比べて製造コストは低いものの、磁化の温度係数の絶対値が大きいためにセンサの構成材料としては使用できないという課題があった。また、アルニコ磁石(A1-Ni-Co-Fe系磁石)は、磁化の温度係数の絶対値が小さく、製造コストが低いものの、保磁力が小さいために実用が困難であった。このため、低コストでフェライト磁石以上の硬磁気特性を少なくとも備え、さらには温度特性が優れた硬磁性材料の出現が望まれていた。

【0004】そこで、本願発明者らは、低コストで高い

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硬磁気特性を示す硬磁性材料を得るために特願平8-68822号、特願平8-242356などにおいて特許出願を行っている。これらの特許出願に記載された技術によれば、Feを主成分とし、Zr、Nb、Ta、Hf、Ti、V、Mo、Wのうち1種または2種以上からなる元素Mと、希土類元素のうちの1種または2種以上からなる元素Rと、Bとを含む非晶質合金を液体急冷法を用いて作製した後、該非晶質合金を600～900℃で熱処理して、bccのFeと、Fe-Bの化合物および/または $R_2Fe_{14}B$ を主体とする平均結晶粒径100nm以下の微細結晶相を析出させることで、残留磁化(Ir)が0.8～1.3T、保磁力(iHc)が170～300kA/m、最大磁気エネルギー積((BH)max)が60～110kJ/m<sup>3</sup>の比較的高い硬磁気特性を示す硬磁性材料が製造できる。以上のような合金の研究の基で本願発明者らは、低コストで、硬磁気特性が優れ、しかも温度特性が優れた硬磁性材料を製造するために、種々の検討及び実験を重ねた結果、パーミアンス係数(p)と磁化の温度係数とは相関があることを発見し、本発明に到達したのである。

【0005】本発明は上記事情に鑑みてなされたもので、低コストで、硬磁気特性が優れ、しかも温度特性が優れた硬磁性材料を提供することを目的とする。

【0006】

【課題を解決するための手段】上述の課題を解決するために、本発明は、以下の構成を採用した。本発明の硬磁性材料は、Fe、Co、Niのうちの1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含む合金からなり、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下であり、保磁力が1kOe以上であることを特徴とする。また、本発明の硬磁性材料は、保磁力1kOe以下のソフト磁性相または準ハード磁性相と、保磁力1kOe以上のハード磁性相とをそれぞれ10vol(体積)%以上含む合金からなり、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下であり、保磁力が1kOe以上であることを特徴とする。更に、本発明の硬磁性材料は、キュリー温度が600℃以上の磁性相とキュリー温度が600℃以下の磁性相とをそれぞれ10vol(体積)%以上含む合金からなり、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下であり、保磁力が1kOe以上であることを特徴とする。

【0007】本発明の硬磁性材料は、Fe、Co、Niのうちの1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含む合金からなり、保磁力の温度係数の絶対値が0.35%/K以下であり、保磁力が1kOe以上であることを特徴とする。また、本発明の硬磁性材料は、保磁力1kOe以下のソフト磁性相



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あるいはパーミアンス線は、磁石の形状に依存し、磁化方向の長さが短くなると、小さくなり、長くなると大きくなるものであり、例えば、 $p=1.5$ のものは円盤形であり、 $p=10$ のものは角柱形である。パーミアンス係数 ( $p$ ) と反磁界係数 ( $N$ ) との間には、下記式

(1)

$$p = (1 - N) / N \quad \dots (1)$$

で示される関係がある。従って、減磁曲線と磁石材料の形状が与えられると、その動作点 ( $B$ 、 $H$ ) は決定される。その磁石材料が外部につくる静磁界のエネルギー

(U) は、下記式 (2)

$$U = BHV / 2 \quad \dots (2)$$

(式中、 $V$ は磁性材料の体積) で与えられる。磁石材料の形状が変化すると、反磁界、すなわちパーミアンス線が変化するので、動作点  $p$  が変化し上記  $U$  の値が変化する。途中ある動作点  $p_m$  で  $U$  の値が最大となり、そのときの ( $BH$ ) の積が最大磁気エネルギー積 ( $(BH)_{max}$ ) である。

【0016】本発明に係る硬磁性材料をセンサ等を使用する場合は、温度変化に起因して出力にドリフトが生じるのを防止するために温度特性が優れるものすなわち磁化の温度係数の絶対値が小さいものを用いることが好ましく、本発明の硬磁性材料は上述のようにパーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が  $0.15\%/K$  以下と小さいものであるもので、センサ等に使用することができる。また、本発明に係る硬磁性材料を、パーミアンス係数が小さい値、例えばパーミアンス係数が2以下の形状で使用した場合においては、硬磁性材料の硬磁気特性は、磁化の温度係数よりも保磁力の温度係数に影響されるために、保磁力の温度係数が小さいものを用いることが好ましく、本発明の硬磁性材料は、上述のように保磁力の温度係数の絶対値が  $0.35\%/K$  以下、特に室温  $\sim 100^\circ C$  の温度範囲で  $0.30\%/K$  と小さいものであるもので、特に小型のセンサ等を使用することができる。また、本発明の硬磁性材料は、パーミアンス係数が2以上となるような形状で使用したときの磁化の温度係数の絶対値が  $0.10\%/K$  以下となるものが、温度特性がより優れる点でより好ましい。更に、本発明の硬磁性材料は、パーミアンス係数が10以上となるような形状で使用するのが、磁化の温度係数の絶対値が  $0.08\%/K$  以下と温度特性がより優れる点でより好ましい。

【0017】本発明の硬磁性材料は、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が  $0.15\%/K$  以下、より好ましくは  $0.10\%/K$  以下と従来型  $Nd-Fe-B$  系磁石と同等かそれより小さいものを実現することができる。さらに、本発明の硬磁性材料は、アルニコ磁石より保磁力 ( $iHc$ ) が大きく、また、従来から温度特性が良好なものとして使用されている  $Sm-Co$  系磁石よりも安価である。ま

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た、本発明の硬磁性材料は、従来の  $Nd-Fe-B$  系の磁石をパーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が  $0.11 \sim 0.15\%/K$  に対して、パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が  $0.08\%/K$  以下と小さいものを実現することができる。更に、本発明の硬磁性材料は、従来の  $Nd-Fe-B$  系の磁石の保磁力の温度係数の絶対値が  $0.35 \sim 0.4\%/K$  であるのに対して、保磁力の温度係数の絶対値が  $0.35\%/K$  以下と小さいものを実現することができる。特に、室温  $\sim 100^\circ C$  の温度範囲での保磁力の温度係数の絶対値を  $0.30\%/K$  以下と小さくすることができる。本発明の硬磁性材料は、特に、後述するように  $Si$  を  $T$  元素置換で  $0.5 \sim 5$  原子%添加あるいは  $T$  元素中に  $Co$  が  $0.5 \sim 20\%$  含まれるようにすることにより、温度特性が優れた硬磁性材料を好適に実現することができる。

【0018】また、本発明の硬磁性材料は、保磁力  $1kOe$  以下のソフト磁性相または準ハード磁性相と、保磁力  $1kOe$  以上のハード磁性相とをそれぞれ  $10vol$  (体積)%以上含み、保磁力 ( $iHc$ ) が  $1kOe$  以上のものであってもよい。このように保磁力  $1kOe$  以下のソフト磁性相または準ハード磁性相と、保磁力  $1kOe$  以上のハード磁性相を上述の範囲で含んでいると、ソフト磁性相とハード磁性相のそれぞれの特性を備えることができる点で好ましい。保磁力  $1kOe$  以下のソフト磁性相または準ハード磁性相が  $10vol$  (体積)%未満であると、ハード磁性相に必要な  $Nd$  などが多くなり、また、残留磁化 ( $I_r$ ) も低下するので好ましくない。また、保磁力  $1kOe$  以上のハード磁性相が  $10vol$  (体積)%未満であると、保磁力 ( $iHc$ ) が低くなるため好ましくない。保磁力  $1kOe$  以下のソフト磁性相または準ハード磁性相の好ましい含有量は  $20 \sim 60vol$  (体積)%であり、保磁力  $1kOe$  以上のハード磁性相の好ましい含有量は  $40 \sim 80vol$  (体積)%である。

【0019】更に、本発明の硬磁性材料は、保磁力  $1kOe$  以下のソフト磁性相と保磁力  $1kOe$  以上のハード磁性相とをそれぞれ  $10vol$  (体積)%以上含み、保磁力の温度係数の絶対値が  $0.35\%/K$  以下であり、保磁力が  $1kOe$  以上のものであってもよい。このように保磁力  $1kOe$  以下のソフト磁性相と保磁力  $1kOe$  以上のハード磁性相を上述の範囲で含んでいると、上述と同様に、ソフト磁性相とハード磁性相のそれぞれの特性を兼ね備えることができる。

【0020】また、本発明の硬磁性材料は、キュリー温度が  $600^\circ C$  以上の磁性相とキュリー温度が  $600^\circ C$  以下の磁性相とをそれぞれ  $10vol$  (体積)%以上含み、保磁力が  $1kOe$  以上のものであってもよく、このようにキュリー温度が  $600^\circ C$  以上の磁性相とキュリー

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温度が600℃以下の磁性相を上述の範囲で含んでいるとソフト磁性相とハード磁性相のそれぞれの特性を兼ね備えることができる点で好ましい。それは、bcc-Fe相のキュリー温度は770℃付近であり、 $R_2Fe_{14}B$ 相のキュリー温度が315℃付近であることから、本発明の硬磁性材料が磁化に関与する相であるソフト磁性相とハード磁性相との2相を有するためには、キュリー温度が600℃以上の磁性相とキュリー温度が600℃以下の磁性相とを含む必要がある。キュリー温度が600℃以上の磁性相が10vol(体積)%未満であると、比較的高いパーミアンスで使用したときの磁化の温度変化が大きくなるため好ましくない。また、キュリー温度が600℃以下の磁性相が10vol(体積)%未満であると、ハード磁性相が少なくなるため、保磁力(iHc)が低くなり好ましくない。キュリー温度が600℃以上の磁性相の好ましい含有量は、20~60vol(体積)%であり、キュリー温度が600℃以下の磁性相の好ましい含有量は40~80vol(体積)%である。

【0021】また、本発明の硬磁性材料は、平均結晶粒径100nm以下の微細結晶質相を主体として含んでおり、この微細結晶質相には、平均結晶粒径100nm以下のbcc-Fe相と、平均結晶粒径100nm以下の $R_2Fe_{14}B$ 相が析出している。さらに、本発明の硬磁性材料は、上記のbcc-Fe相と $R_2Fe_{14}B$ 相の微細結晶質相と、残留した非晶質相とのナノ複相組織を形成している。また、本発明の硬磁性材料は、上記の構成の合金溶湯を急冷することにより得られた非晶質相を主相とする合金が熱処理されてなるものであってもよい。特に、上記の構成の合金溶湯を急冷して得られた非晶質相を主相とする合金が、少なくとも結晶質相の初相が析出する温度範囲において10K/分以上の昇温速度で熱処理されてなるものであることが、bcc-Fe相の平均粒径を細かくし、硬磁気特性を向上させる点で好ましい。本発明の硬磁性材料の多くは、bcc-Fe相または $Fe_3B$ 相または $Fe_2B$ 相が、熱処理によって他の相( $R_2Fe_{14}B$ 相)よりも早く析出するいわゆる初相である。

【0022】さらに、本発明に係る硬磁性材料は、保磁力(iHc)が2kOe以上のものであることが好ましい。また、本発明に係る硬磁性材料は、飽和磁化(I<sub>s</sub>)に対する残留磁化(I<sub>r</sub>)の割合(I<sub>r</sub>/I<sub>s</sub>)が、0.6以上のものであることが好ましい。ここで、本発明において飽和磁化(I<sub>s</sub>)は試料に15kOe以上の磁場をかけたときに得られるほぼ飽和した磁化の値を意味する。上述のような硬磁性材料中の結晶質相の平均結晶粒径、および各相中における各原子の濃度の制御は、非晶質を主相とする合金を熱処理して硬磁性材料を得る際の熱処理条件を制御することによって実現できる。熱処理条件は、昇温速度、熱処理温度(アニール温

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度)及びその保持時間などである。

【0023】本発明に係る硬磁性材料は、以下の組成式で表すことができる。

$$TxMyRzBw$$

上記組成式中のTは、基本的に全体から元素M、R、Bの含有量を差し引いた残部であるが、Fe、Co、Niのうち1種以上の元素を表わす。これらの元素Tは、本発明に係る硬磁性材料の主成分であり、磁性を担う元素であるため、元素Tの組成比xは50原子%以上である。元素Tの組成比xを増加させると、それに伴って飽和磁化(I<sub>s</sub>)が増加する。100emu/g以上の高い残留磁化(I<sub>r</sub>)を実現するためには、飽和磁化(I<sub>s</sub>)が少なくとも130emu/gは必要であり、これを満たすには元素Tの組成比xは80原子%以上であるのが望ましく、86原子%以上であるのがより望ましい。また、良好な硬磁気特性を得るためには93原子%以下とするのが好ましい。本発明の硬磁性材料においては、元素Tの少なくとも一部としてFeが含まれていることが必要である。

【0024】上記組成式中のMは、Zr、Nb、Ta、Hf、Ti、V、Mo、Wのうち1種以上の元素を表わし、これらの元素Mは非晶質形成能が高いものである。本発明に係る硬磁性材料において、元素Mを添加することにより、元素R(希土類元素)が低濃度の場合でも非晶質相を形成することができる。元素R置換で元素Mの組成比yを増加させると、それに伴って残留磁化(I<sub>r</sub>)は増加するが、保磁力(iHc)が低下し、硬磁気特性から軟磁気特性へと変化する。また、磁性を担う元素T置換で元素Mを増加させると、飽和磁化(I<sub>s</sub>)、残留磁化(I<sub>r</sub>)の減少が生じる。従って、良好な硬磁気特性を得るために、元素Mの組成比yは0原子%以上15原子%以下の範囲とするのが好ましく、1原子%以上5原子%以下の範囲であることがより好ましい。また、1原子%以上3原子%以下とすると更に好ましい。

【0025】上記組成式中のRは、希土類元素(Sc、Y、La、Ce、Pr、Nd、Pm、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm、Yb、およびLu)のうちの1種以上の元素を表わす。元素RとFeとBとを含む非晶質を主相とする合金を873~1173K(600~900℃)の範囲の適切な温度で加熱したときに析出する金属間化合物 $R_2Fe_{14}B$ は、本発明の硬磁性材料に優れた硬磁気特性を付与するものである。元素Rの組成比zを増加させると、それに伴って飽和磁化(I<sub>r</sub>)が減少する。100emu/g以上の高い残留磁化(I<sub>r</sub>)を得るためには、飽和磁化(I<sub>s</sub>)が少なくとも130emu/gは必要であり、これを満たすためには元素Rの組成比zは20原子%以下であることが望ましい。また元素Rは非晶質を形成し易い元素であり、元素Rの組成比zが小さ過ぎると良好な非晶質相または微細結晶相を得られないため、元素Rの組成比zと



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しては3原子%以上とするのが望ましく、高い飽和磁化(I<sub>r</sub>)と保磁力(i<sub>Hc</sub>)を両立させるためには、10原子%以下、更に好ましくは7原子%以下とすると良い。さらに元素Rの一部または全部をNdおよび/またはPrで構成すると、さらに高い硬磁気特性が得られる。

【0026】上記組成式中のBは、非晶質を形成し易い元素である。また、元素RとFeとBとを含む非晶質相を873~1173K(600~900℃)の範囲の適切な温度で熱処理したときに析出する化合物R<sub>2</sub>Fe<sub>14</sub>Bは、本発明の硬磁性材料に硬磁気特性を付与するものである。良好な非晶質相または微細結晶質相を得るためには、Bの濃度を2原子%以上とするのが望ましいが、Bの組成比wの増加に伴って飽和磁化(I<sub>s</sub>)、残留磁化(I<sub>r</sub>)、および保磁力(i<sub>Hc</sub>)が減少するので、良好な硬磁気特性を得るために、Bの組成比wを20原子%以下、より好ましくは7原子%以下、更に好ましくは5原子%以下とするのが望ましい。

【0027】また、本発明の硬磁性材料には、Cr、Al、Pt、Ru、Rh、Pd、Os、Ir、Cu、Ag、Au、Ga、Geのうち1種以上の元素Eが添加されていてもよく、その場合の硬磁性材料は、下記の組成式で表すことができる。

$T_xMyR_zBwEv$

この場合の磁性を担う元素Tの組成比xは、基本的に全体から元素M、R、B、Eの含有量を差し引いた残部であるが、飽和磁化(I<sub>s</sub>)を増加させる点から好ましくは50原子%以上、より好ましくは80原子%以上93原子%以下の範囲であり、100emu/g以上の高い残留磁化(I<sub>r</sub>)と高い保磁力(i<sub>Hc</sub>)の両立を実現するためには86原子%以上93原子%以下の範囲とするのが好ましい。上記組成式中の元素Mの組成比yは、良好な硬磁気特性を得るために、好ましくは0原子%以上15原子%以下、より好ましくは1原子%以上5原子%以下の範囲であり、100emu/g以上の高い残留磁化(I<sub>r</sub>)を実現するためには、1原子%以上3原子%以下の範囲とすることが好ましい。なお、より高い残留磁化(I<sub>r</sub>)を得るためには、組成比を0.5原子%以上1原子%以下としても良い。

【0028】上記組成式中の元素Rの組成比zは、本発明の硬磁性材料に優れた硬磁気特性を付与するためと、良好な非晶質相または微細結晶質相を得るために、好ましくは3原子%以上20原子%以下、より好ましくは3原子%以上10原子%以下の範囲であり、100emu/g以上の高い残留磁化(I<sub>r</sub>)を実現するためには、3原子%以上7%以下の範囲とするのが好ましい。上記組成式中のBの組成比wは、良好な非晶質相または微細結晶質相を得るために2原子%以上とするのが望ましいが、良好な硬磁気特性を得るためには、Bの組成比wを20原子%以下、より好ましくは7原子%以下、更に好

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ましくは5原子%以下とするのが望ましい。元素Eが添加されることによって硬磁性材料の耐食性が向上、もしくは、結晶組織の微細化を促進させることができる。従って、元素Eの組成比vは、0.1原子%以上であることが好ましい。ただし、元素Eの組成比vが高過ぎると硬磁気特性が劣化するので、元素Eの組成比vは、好ましくは10原子%以下、より好ましくは5原子%以下とされる。また、100emu/g以上の高い残留磁化(I<sub>r</sub>)を達成するためには、元素Eを添加しない方が好ましい。

【0029】本発明の硬磁性材料において、元素T中にFe以外にCoが含まれるようにすれば、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値、パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値及び保磁力の温度係数の絶対値を小さくすることができる点で好ましい。その理由は、元素T中にCoが含まれているとキュリー温度が上昇するので、磁化や保磁力の温度変化が小さくなり、また、磁化の角型比が高くなるため磁気特性の温度変化が小さくなり、さらに、このCoはbcc-Fe相にも含まれるので、残留磁化の温度変化が小さくなるからである。Coの含有量は、多過ぎると磁気特性を劣化させるので、好ましくは50原子%以下、より好ましくは0.5原子%以上30原子%以下、さらに好ましくは0.5原子%以上20原子%以下の範囲とされ、合金の組成や熱処理条件等に応じて適宜設定するのが好ましい。

【0030】また、本発明の硬磁性材料において、Siを元素T置換で添加すれば、磁気特性、特に保磁力(i<sub>Hc</sub>)、および最大磁気エネルギー積((BH)<sub>max</sub>)をさらに向上させることができ、また、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値、特に、パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値を低くすることができる。Siの添加量は、多過ぎると元素Tの組成比が低くなるために硬磁性材料の磁気特性がかえって低下するので、好ましくは0.5原子%以上5原子%以下、より好ましくは0.5原子%以上3原子%以下の範囲とされ、合金の組成や熱処理条件等に応じて適宜設定するのが好ましい。このようにして保磁力(i<sub>Hc</sub>)および温度特性が改善された硬磁性材料は、特に、小型モータ用磁石、センサとして好適に用いられる。

【0031】つぎに、本発明に係る硬磁性材料は、以下のようにして製造することができる。上述のような非晶質を主相とする合金を得る方法は、回転ドラムに合金溶湯を吹き付けて急冷して薄帯状に形成する方法、合金溶湯を冷却用気体中に噴出して液滴状態で急冷して粉末状に形成する方法などの液体急冷法、あるいはスパッタリングやCVD法による方法等を用いることができる。また、上記非晶質を主相とする合金に対する熱処理は、任

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意の加熱手段を用いて行なうことができ、例えば本発明の硬磁性材料からなる圧密体を得る場合には、まず非晶質を主相とする合金を粉末状にし、その合金粉末をホットプレスにより加圧成形すると同時に適切な昇温速度および熱処理温度（アニール温度）で熱処理する方法を好ましく用いることができる。

【0032】熱処理時の昇温速度は、10 K/分以上、好ましくは100 K/分以上の範囲で、非晶質を主相とする合金の組成により好ましく設定される。熱処理時の昇温速度が10 K/分未満であると、熱処理により合金中に析出する結晶粒が粗大化して、ソフト磁性相（bcc（体心立方構造）-Fe）とハード磁性相（ $R_2Fe_{14}B$ ）の交換結合特性が低下し、硬磁気特性が劣化するので好ましくない。また、熱処理時の昇温速度を100 K/分以上の範囲とすることにより、微細組織の均一化による特性向上や、熱処理工程や製造工程に要する時間の短縮化が可能となる。なお、昇温速度の上限としては、装置上の制約から、200 K/分程度とされる。

【0033】特に、非晶質相を主相とする合金を熱処理する時の昇温速度を、少なくとも結晶質相の初相が析出する温度範囲において10 K/分以上、より好ましくは50 K/分以上とすることにより、更に優れた硬磁気特性が得られる。本発明に係る硬磁性材料においては、熱処理によって析出する結晶相にはbcc-Fe相（ソフト磁性相）、 $R_2Fe_{14}B$ （ハード磁性相）及び $Fe_3B$ 相が含まれ、これらの結晶相のうちで最も低い温度で析出する相（初相）は、例えばbcc-Fe相または $Fe_3B$ 相または $Fe_2B$ 相等であり、このいずれかが初相になるか、あるいはその析出する温度は、非晶質相を主相とする合金の組成によって異なり、例えば500～650℃の範囲内である。また、bcc-Fe相が初相として析出することが最も好ましい。この温度範囲内における昇温速度が10 K/分未満であると、熱処理により合金中に析出するbcc-Fe相の結晶粒が粗大化するため、ソフト磁性相（bcc（体心立方構造）-Fe）とハード磁性相（ $R_2Fe_{14}B$ ）の交換結合特性が低下し、硬磁気特性が劣化するため好ましくない。また、結晶質相の初相が析出する温度範囲での昇温速度を50 K/分以上の範囲とすることにより、bcc-Fe相の結晶粒の粒径をより微細化することが可能となり、均一な微細組織の結晶相が形成できる。

【0034】上述の非晶質相を主相とする合金の組織内では、合金組成のゆらぎ、即ち合金組成の濃度の差が大きい。熱処理時にはこれらのゆらぎの部分を核として結晶相の初相（bcc-Fe相）が成長する。このとき、昇温速度が大きいと、核の発生確率が高くなり、bcc-Fe相の結晶粒が合金組織内で数多く析出する。結晶粒径は、昇温速度に依存するので、bcc-Fe相の粒径は昇温速度が大きいほど小さくなる。更に、昇温を続けると、bcc-Fe相の粒界の部分から $R_2Fe_{14}B$

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相が析出し始める。このときの昇温速度は必ずしも10 K/分以上にする必要はない。 $R_2Fe_{14}B$ 相の粒径の昇温速度の依存性はbcc-Fe相の場合よりも大きく、昇温速度が大きいほど粒径が小さくなる傾向にあるが、本発明においては、bcc-Fe相の結晶粒が既に数多く析出しており、合金組織におけるbcc-Fe相の結晶粒の占める体積が大きくなっているために、 $R_2Fe_{14}B$ 相が析出するスペースが相対的に小さくなり、 $R_2Fe_{14}B$ 相が析出する温度範囲における昇温速度が10 K/分未満であっても、 $R_2Fe_{14}B$ 相の粒径が小さくなる。つまり、 $R_2Fe_{14}B$ 相の粒径は、初相（bcc-Fe相）の析出する温度範囲での昇温速度に大きく依存している。このようにして、本発明における硬磁性材料においては、多数のbcc-Fe相の結晶粒の周辺に、 $R_2Fe_{14}B$ 相の結晶粒が多数析出した形態となり、bcc-Fe相と $R_2Fe_{14}B$ 相との交換結合特性が向上し、硬磁気特性が向上するものと考えられる。

【0035】熱処理時の熱処理温度（アニール温度）は、好ましくは873～1173 K（600～900℃）、より好ましくは973 K～1023 K（700～800℃）の範囲、保持時間（熱処理時間）は好ましくは0～60分、より好ましくは3～10分の範囲で、非晶質相を主相とする合金の組成により好ましく設定される。熱処理温度が873 K（600℃）未満であると、硬磁気特性を担う $R_2Fe_{14}B$ 相の析出量が少ないため十分な硬磁気特性が得られず、好ましくない。一方、熱処理温度が1173 K（900℃）を越えると、他の析出物が析出して硬磁気特性が低下してしまうため好ましくない。

【0036】図1は、本発明の硬磁性材料をホールポテンシオメータ用磁石に適用した実施形態の例を示す斜視図である。図中符号1は上述の本発明に係る硬磁性材料からなる磁石部、2はこの磁石部1を支持するための支持部である。上記磁石部1は、パーミアンス係数が約5程度となる形状に成形された扇形のものであり、磁化の温度係数の絶対値が0.13%/K以下であり、保磁力の温度係数の絶対値が0.35%/K以下のものである。上記支持部は、磁石部1を収納するための切り欠き部3を有する円盤部4と、この円盤部4の頂部から突出して設けられた円柱状の接続部5からなるものである。

【0037】実施形態のホールポテンシオメータ用磁石にあっては、本発明に係る硬磁性材料性からなる磁石部1が用いられたことにより、従来のフェライト磁石やNd-Fe-B系磁石より温度特性が同等かまたは優れており、温度変化に起因する出力のドリフトを防止することができるので、電子機器の回路電圧の精度良く調整することができる。また、実施形態のホールポテンシオメータ用磁石にあっては、従来のSm-Co系磁石やNd-Fe-B系磁石より低コストであり、従来のフェライ

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トやアルニコ磁石より硬磁気特性が優れる。

【0038】図2は、本発明の硬磁性材料を磁気式ロータリーエンコーダ用磁石に適用した実施形態の例を示す斜視図である。図中符号10は、実施形態の磁気式ロータリーエンコーダ用磁石である。この実施形態の磁気式ロータリーエンコーダ用磁石10は、上述の本発明に係わる硬磁性材料からなり、パーミアンス係数が約2程度となる形状に成形された円盤状のものであり、その円周に沿って多極に着磁されてなるものである。また、このロータリーエンコーダ用磁石10は、磁化の温度係数の絶対値が0.15%/K以下のものである。実施形態の磁気式ロータリーエンコーダ用磁石10にあっては、本発明に係わる硬磁性材料性が用いられたことにより、従来のフェライト磁石やNd-Fe-B系磁石より温度特性が同等かまたは優れており、温度変化に起因する出力のドリフトを防止することができるので、電子機器の回転角度等を精度良く検出することができる。また、実施形態の磁気式ロータリーエンコーダ用磁石10にあっては、従来のSm-Co系磁石やNd-Fe-B系磁石より低コストであり、従来のフェライトやアルニコ磁石より硬磁気特性が優れる。

【0039】図3は、本発明の硬磁性材料をスピーカ用磁石に適用した実施形態の第一の例を示す断面図である。図中符号21は鉄からなるポールピース、22は該ポールピース21の外方に隙間を隔てて設けられた円筒状の圧粉磁心（ヨーク）、23、24はポールピース21とヨーク22の隙間の上下にそれぞれ配置された本発明の硬磁性材料からなる磁石、25はコーン状振動板である。上記磁石23、24は、リング状に形成されているものである。これら磁石23、24により作られる磁気ギャップ間には音声コイル（図示略）が配置されており、さらにこの音声コイルはコーン状振動板25に接続されている。この音声コイルに増幅器からの音声電流が流れると、それに応じて運動を起し、これに接続されているコーン状振動板25を動かし、音として放射することができる。

【0040】第一の例のスピーカ用磁石にあっては、本発明に係る硬磁性材料性からなる磁石23、24が用いられたことにより、従来のフェライト磁石やNd-Fe-B系磁石より温度特性が優れており、温度変化に起因する出力のドリフトを防止することができるので、音声電流を精度良くボイスコイルに流すことができる。また、第一の例のスピーカ用磁石にあっては、従来のSm-Co系磁石やNd-Fe-B系磁石より低コストであり、従来のフェライトやアルニコ磁石より硬磁気特性が優れる。

【0041】図4は、本発明の硬磁性材料をスピーカ用磁石に適用した実施形態の第二の例を示す断面図である。図中符号31、32は対向配置された上下一対の鉄からなるポールピース、33は該ポールピース31、3

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2の間に配設された本発明の硬磁性材料からなる磁石、34はこれらのポールピース31、32及び磁石33の外方に隙間を隔てて設けられた円筒状のヨーク、35はコーン状振動板であり、36は磁気シールドカバーである。上記磁石33は、リング状に形成されたものである。上記ポールピース31、32、磁石33は、ボルト37、ワッシャー38、ナット39により磁気シールドカバー36に取り付けられている。第二の例のスピーカ用磁石にあっては、本発明に係る硬磁性材料性からなる磁石33が用いられたことにより、上述の第一の例のスピーカ用磁石と略同様の効果がある。

【0042】上述の硬磁性材料は、特に、Fe、Co、Niのうち1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bを含む合金からなり、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下のものである。従来のフェライトやNd-Fe-B系磁石より温度特性が同等かまたは優れており、従って、センサ等に利用した場合に温度変化に起因する出力のドリフトを防止することができるので、検出精度の信頼性を向上させることができる。また、パーミアンス係数が2以下となるような形状で使用した場合においては、硬磁性材料の温度特性は保磁力の温度係数に大きく影響されるが、上述の硬磁性材料は、保磁力の温度係数の絶対値が0.35%/K以下と小さいので、従来のNd-Fe-B系磁石より温度特性が同等かまたは優れており、小型の磁気センサ、ロータリーエンコーダ等に使用した場合には、温度変化に起因する出力のドリフトを防止することができるので、検出精度の信頼性を向上させることができる。

【0043】また、本発明に係る硬磁性材料は、平均結晶粒径100nm以下の微細結晶質相を主体として含んでおり、この微細結晶質相には、平均結晶粒径100nm以下のbcc-Fe相と、平均結晶粒径100nm以下の $R_2Fe_{14}B$ 相が析出している。ソフト磁性相（bcc（体心立方構造）-Fe）とハード磁性相（ $R_2Fe_{14}B$ ）の交換結合特性が向上しており、残留磁化（ $I_r$ ）、角型比（ $I_r/I_s$ ）、保磁力（ $iH_c$ ）、最大磁気エネルギー積（ $(BH)_{max}$ ）が増加し、優れた硬磁気特性が得られる。具体的には、残留磁化（ $I_r$ ）が100emu/g以上、好ましくは130emu/g以上の硬磁性材料、角型比（ $I_r/I_s$ ）が0.6以上、好ましくは0.7以上の硬磁性材料、保磁力（ $iH_c$ ）が1kOe以上、好ましくは2kOe以上の硬磁性材料、最大磁気エネルギー積（ $(BH)_{max}$ ）が100kJ/m<sup>3</sup>を越える優れた硬磁性材料を実現することができる。

【0044】さらに、本発明に係る硬磁性材料は、希土類元素Rの含有量を少なくとも優れた硬磁気特性が得られるので、Sm-Co系磁石やNd-Fe-B系磁石

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に比べて比較的低い製造コストで製造することができる。

【0045】また、上述の硬磁性材料は、急冷直後において非晶質相を主相とする合金を熱処理して微細な結晶相を析出させたものであり、特に、熱処理する際の昇温速度が、結晶質相の初相が析出する温度範囲において10K/分以上とすることにより、bcc-Fe相の結晶粒が多数形成し、その結晶粒の肥大化を防ぐことができると共に、後から生成する $R_2Fe_{14}B$ 相の結晶粒の肥大化も防げるので、上記合金中に析出する微細結晶質相のbcc-Fe相と $R_2Fe_{14}B$ 相の平均結晶粒径を微細化することができる。

【0046】さらに、 $R_2Fe_{14}B$ 相においては、元来bcc-Fe相と同程度の微細な平均結晶粒径を有しており、また、bcc-Fe相の結晶粒が $R_2Fe_{14}B$ 相が析出する以前に多数生成し、 $R_2Fe_{14}B$ 相が析出するスペースが小さくなっているため、 $R_2Fe_{14}B$ 相の結晶粒の大きさは、 $R_2Fe_{14}B$ 相の析出する温度領域における昇温速度に依存せず、初相(bcc-Fe相)の析出する温度領域における昇温速度に依存している。つまり、初相(bcc-Fe相)の析出する温度領域で昇温速度を速くすることにより、 $R_2Fe_{14}B$ 相の平均結晶粒径が微細化される。従って、bcc-Fe相の結晶粒と $R_2Fe_{14}B$ 相の結晶粒との隣り合う確率が高くなり、ソフト磁性相(bcc(体心立方構造)-Fe)とハード磁性相( $R_2Fe_{14}B$ )の交換結合が行われ易くなるために交換結合特性が向上し、残留磁化( $I_r$ )、角型比( $I_r/I_s$ )、保磁力( $iH_c$ )、最大磁気エネルギー積( $(BH)_{max}$ )が増加し、優れた硬磁気特性が得られる。

【0047】また、本発明に係る硬磁性材料にあつては、Si元素をT元素置換で0.5~5原子%添加、あるいはT元素中にFe以外にCoが0.5~50%含まれるようにすることにより、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下のもの、特に、パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が0.1%/K以下のものを実現することができる。従って、本発明に係る硬磁性材料は、磁気式ロータリーエンコーダや

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力、モータなどに好適に用いることができる。

【0048】

【実施例】(実験例1) 以下のようにして、各種組成の急冷薄帯合金を熱処理して硬磁性材料を作製した。まず、アーク溶解法によりインゴットを作製し、Ar雰囲気中において回転しているCuロール上に、溶解した金属をスリット径約0.3mmの細幅ノズルから吹出すことにより、約20 $\mu$ mの厚さの急冷薄帯合金を作製した。次いで、得られた急冷薄帯合金を $1 \times 10^{-2}$ Pa以下の赤外線イメージ炉中において、昇温速度180K/分で加熱し、アニール温度1023K(750℃)で約180秒間保持する条件で熱処理して得られる薄帯合金試料(実施例)を得た。ここで得られた薄帯合金試料の組成は、いずれも本発明の範囲内にある $Fe_{76}Co_{10}Nb_2Pr_7B_5$ なる組成の薄帯合金、 $Fe_{66}Co_{20}Nb_2Pr_7B_5$ なる組成の薄帯合金、 $Fe_{84}Nb_2Pr_7B_5Si_2$ なる組成の薄帯合金であった。

【0049】得られた実施例の薄帯合金試料について、VSM(振動試料型磁力計)を用いて、10kOeの印加磁場中及び真空中で室温~約490Kにおける減磁曲線(第2象限)を測定した。結果を図5~図7に示す。図5~図7中、イはパーミアンス係数( $p$ )が10(角柱形)である直線であり、ロは $p$ が1.5(円盤形)である直線である。また、減磁曲線(第2象限)より求めた残留磁化( $I_r$ )及び保磁力( $iH_c$ )の温度変化を図8に示す。

【0050】また、表1には、実施例の薄帯合金試料の室温での磁気特性を示す。なお、表1中、 $I_r/I_s$ は飽和磁化( $I_s$ )に対する残留磁化( $I_r$ )の割合(角型比)である。更に、表2には、実施例の薄帯合金試料の室温~約490Kにおける残留磁化及び保磁力の温度係数と、 $p=1.5$ 、 $p=10$ となる形状としたときの残留磁化の温度係数を示す。

【0051】図8には、比較例として従来のフェライト磁石とNd-Fe-B系( $Nd_2Fe_{14}B$ )磁石の磁気特性と温度との関係を示す。また、表2には、これらの従来の磁石の残留磁化及び保磁力の温度係数を合わせて示す。

【0052】

【表1】

磁気特性(室温)

硬磁性材料の組成	$I_s(emu g^{-1})$	$I_r(emu g^{-1})$	$iH_c(kOe)$	$I_r/I_s$
$Fe_{76}Co_{10}Nb_2Pr_7B_5$	147.2	114.8	3.1	0.78
$Fe_{66}Co_{20}Nb_2Pr_7B_5$	156.3	127.1	3.11	0.81
$Fe_{84}Nb_2Pr_7B_5Si_2$	139.3	105.2	3.62	0.755

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【0053】

\* \* 【表2】

Ir及びiHcの温度係数（室温～約490 K）

	硬磁性材料の組成	dIr/dT (%/K)	diHc/dT (%/K)	P=1.5のときの dI/dT(%/K)	P=10のときの dI/dT(%/K)
実施例	Fe <sub>88</sub> Nb <sub>2</sub> Pr <sub>5</sub> B <sub>5</sub>	-0.06	-0.43	-0.38	-0.12
	Fe <sub>76</sub> Co <sub>10</sub> Nb <sub>2</sub> Pr <sub>7</sub> B <sub>5</sub>	-0.02	-0.28	-0.20	-0.10
	Fe <sub>66</sub> Co <sub>20</sub> Nb <sub>2</sub> Pr <sub>7</sub> B <sub>5</sub>	-0.02	-0.36	-0.33	-0.08
	Fe <sub>84</sub> Nb <sub>2</sub> Pr <sub>7</sub> B <sub>5</sub> Si <sub>2</sub>	-0.02	-0.32	-0.17	-0.05
比較例	Fe <sub>77</sub> Nd <sub>15</sub> B <sub>8</sub>	-0.16	-0.4	--	--
	(Fe <sub>0.9</sub> Co <sub>0.1</sub> ) <sub>77</sub> Nd <sub>15</sub> B <sub>8</sub>	-0.11	-0.35	--	--
	フェライト磁石	-0.18	--	--	--

【0054】図8及び表2から、実施例の薄帯合金試料ならびに比較例の磁石は、温度の上昇とともに残留磁化（Ir）及び保磁力（iHc）が減少する傾向が認められる。保磁力の温度係数（diHc/dT）については、実施例のFe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub>B<sub>5</sub>なる組成の試料が-0.43%/Kであり、比較例のNd-Fe-B系磁石の値（-0.4%/K）に近い値である。一方、CoやSiを添加した実施例の薄帯合金試料では、-0.28~-0.36%/Kと比較例のFe<sub>77</sub>Nd<sub>15</sub>B<sub>8</sub>の磁石よりも小さい値であることが認められる。このように、Coを添加することによって保磁力の温度係数が減少するのは、ハード磁性相のキュリー温度が上昇することに起因するものと考えられる。

【0055】次に、残留磁化の温度係数（dIr/dT）については、実施例のFe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub>B<sub>5</sub>なる組成の試料が-0.06%/Kであり、比較例のNd-Fe-B系磁石（Fe<sub>77</sub>Nd<sub>15</sub>B<sub>8</sub>、（Fe<sub>0.9</sub>Co<sub>0.1</sub>）<sub>77</sub>Nd<sub>15</sub>B<sub>8</sub>なる組成の磁石）の値が-0.11~-0.16%/Kであるのに比べて低くなっている。これは、比較例の磁石では磁化に関与する相がハード磁性相のみであるに対して、実施例の薄帯合金試料では、ハード磁性相と、磁化の温度変化率の小さいソフト磁性相（bcc-Fe相）が混在したナノ複相組織を有しているからであると考えられる。また、CoやSiを添加した実施例の薄帯合金試料では、Irの温度係数が-0.02%/Kと大幅に小さい値であることが認められる。図6から、Fe<sub>66</sub>Co<sub>20</sub>Nb<sub>2</sub>Pr<sub>7</sub>B<sub>5</sub>なる組成の試料においては、特に、p=10以上の領域で磁化の温度変化が小さく、温度特性が優れていることが分る。

【0056】図9は、実施例の薄帯合金試料をp=1.5、p=10となる形状でそれぞれ使用したときの各温度での残留磁化（Ir）の値を、図5～図7に示す減磁曲線より求めたものである。また、図9には、比較として、従来のSm-Co磁石とNd-Fe-B系磁石（Nd<sub>2</sub>Fe<sub>14</sub>Bなる組成）とをp=1.5、p=10とな

る形状でそれぞれ使用したときの残留磁化（Ir）の温度変化を合わせて示す。図10は、本発明の組成の範囲内にあるFe<sub>88</sub>Nb<sub>2</sub>Nd<sub>5</sub>B<sub>5</sub>なる組成の焼結バルク

（合金圧密体）試料及びFe<sub>88</sub>Nb<sub>2</sub>Pr<sub>7</sub>B<sub>5</sub>なる組成の薄帯合金試料のパーミアンス係数と残留磁化の温度係数との関係を示す。また、図10には、比較として、従来のNd-Fe-B系磁石（Nd<sub>2</sub>Fe<sub>14</sub>Bなる組成）のパーミアンス係数と温度係数との関係を合わせて示す。

【0057】表2及び図8～図10から、p=1.5と低いパーミアンス係数の場合には、Siを添加した実施例であるFe<sub>84</sub>Nb<sub>2</sub>Pr<sub>7</sub>B<sub>5</sub>Si<sub>2</sub>なる組成の試料の磁化の温度係数が-0.17%/Kであり、Coを添加した実施例であるFe<sub>76</sub>Co<sub>10</sub>Nb<sub>2</sub>Pr<sub>7</sub>B<sub>5</sub>なる組成と、Fe<sub>66</sub>Co<sub>20</sub>Nb<sub>2</sub>Pr<sub>7</sub>B<sub>5</sub>なる組成の試料の磁化の温度係数は、それぞれ-0.20%/K、-0.33%/Kであり、また、Fe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub>B<sub>5</sub>なる組成の試料の磁化の温度係数は、-0.38%/Kと各実施例とも従来の材料と同等の比較的高い温度係数を有している。しかし、p=10と高いパーミアンス係数で使用したときには、実施例のFe<sub>88</sub>Nb<sub>2</sub>Nd<sub>5</sub>B<sub>5</sub>なる組成の試料は、磁化の温度係数が-0.12%/Kであり、従来のNd-Fe-B系磁石の磁化の温度係数と同じ程度である。一方、Siを添加した実施例のFe<sub>84</sub>Nb<sub>2</sub>Pr<sub>7</sub>B<sub>5</sub>Si<sub>2</sub>なる組成の試料は-0.05%/Kであり、Coを添加した実施例のFe<sub>66</sub>Co<sub>20</sub>Nb<sub>2</sub>Pr<sub>7</sub>B<sub>5</sub>なる組成の試料は-0.08%/Kとさらに温度による磁気特性の変化が小さいことを示している。また、p=10となる形状で使用したときには、実施例の薄帯合金試料、特に、Fe<sub>66</sub>Co<sub>20</sub>Nb<sub>2</sub>Pr<sub>7</sub>B<sub>5</sub>なる組成の試料は、300～430 K（27～157℃）程度の実用温度範囲において磁化の温度係数の絶対値が小さく、比較例のSm-Co系磁石と同じ程度の優れた温度特性を有しており、比較例のNd<sub>2</sub>Fe<sub>14</sub>B系磁石よりも温度特性が優れていることが分る。

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【0058】表2及び図8～図10から、実施例の試料は、パーミアンス係数が2以上で使用すれば比較例のNd<sub>2</sub>Fe<sub>14</sub>B系磁石の磁化の温度係数の絶対値と同じ程度であるか、あるいは小さく、特に、パーミアンス係数が10以上で使用したとき、磁化の温度係数は0.1%/Kよりも小さな値が得られており、比較例のNd-Fe-B系磁石よりも磁化の温度係数の絶対値が小さく、温度特性が優れていることが分る。

【0059】(実験例2) 実験例1と同様にして、Fe<sub>90</sub>Nb<sub>2</sub>Nd<sub>5</sub>B<sub>3</sub>、Fe<sub>89</sub>Nb<sub>2</sub>Nd<sub>5</sub>B<sub>4</sub>、Fe<sub>89</sub>Nb<sub>2</sub>Nd<sub>4</sub>B<sub>5</sub>、Fe<sub>79</sub>Co<sub>10</sub>Nb<sub>2</sub>Nd<sub>4</sub>B<sub>5</sub>なる組成の薄帯\*

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\*合金試料を得た。得られた薄帯合金試料について、VSM(振動試料型磁力計)を用いて、10kOeの印加磁場中及び真空中で室温～約160℃における減磁曲線(第2象限)を測定し、保磁力の温度係数を求めた。結果を表3に示す。また、表3には、従来のFe<sub>77</sub>Nd<sub>15</sub>B<sub>8</sub>、(Fe<sub>0.9</sub>Co<sub>0.1</sub>)<sub>77</sub>Nd<sub>15</sub>B<sub>8</sub>なる組成の薄帯合金試料の室温～200℃における保磁力の温度係数を合わせて示す。更に、図11には、減磁曲線から得られた温度と保磁力(iHc)との関係を示す。

【0060】

【表3】

硬磁性材料の組成	温度範囲	diHc/dT (%/K)
Fe <sub>90</sub> Nb <sub>2</sub> Nd <sub>5</sub> B <sub>3</sub>	室温～44℃	-0.22
	室温～66℃	-0.22
	室温～86℃	-0.25
	室温～105℃	-0.26
	室温～125℃	-0.27
Fe <sub>89</sub> Nb <sub>2</sub> Nd <sub>5</sub> B <sub>4</sub>	室温～55℃	-0.08
	室温～76℃	-0.09
	室温～94℃	-0.17
	室温～115℃	-0.19
	室温～135℃	-0.21
Fe <sub>89</sub> Nb <sub>2</sub> Nd <sub>4</sub> B <sub>5</sub>	室温～44℃	-0.33
	室温～65℃	-0.31
	室温～86℃	-0.26
	室温～105℃	-0.30
	室温～125℃	-0.31
	室温～146℃	-0.32
Fe <sub>79</sub> Co <sub>10</sub> Nb <sub>2</sub> Nd <sub>4</sub> B <sub>5</sub>	室温～56℃	-0.31
	室温～77℃	-0.28
	室温～97℃	-0.29
	室温～115℃	-0.30
	室温～137℃	-0.30
	室温～158℃	-0.29
Fe <sub>77</sub> Nd <sub>15</sub> B <sub>8</sub>	室温～200℃	-0.40
(Fe <sub>0.9</sub> Co <sub>0.1</sub> ) <sub>77</sub> Nd <sub>15</sub> B <sub>8</sub>	室温～200℃	-0.35

【0061】表3で明らかなように、本実施例の薄帯合金試料は、保磁力の温度係数の絶対値がいずれも0.35%/Kよりも低くなっており、保磁力の温度変化が小さいことがわかる。特に、室温～約100℃での保磁力の温度係数の絶対値が0.30%/K以下となり、温度特性に優れていることがわかる。一方、従来のFe<sub>77</sub>Nd<sub>15</sub>B<sub>8</sub>、(Fe<sub>0.9</sub>Co<sub>0.1</sub>)<sub>77</sub>Nd<sub>15</sub>B<sub>8</sub>なる組成の薄帯合金試料については、保磁力の温度係数の絶対値がそれぞれ0.4%/K、0.35%/Kであり、本実施例の薄帯合金試料よりも大きくなっている。また、図11から明らかなように、温度の上昇とともに保磁力(iH

c)が緩やかに低下している。従って、このような薄帯合金試料(永久磁石)を磁気センサに用いた場合には、磁気センサの作動温度が急激に上昇しても、保磁力(iHc)の変化が小さいために、磁気センサからの出力のドリフトを小さくすることができる。

【0062】(実験例3) 実験例1と同様にして、Fe<sub>88</sub>Nb<sub>2</sub>Nd<sub>5</sub>B<sub>5</sub>なる組成の急冷薄帯合金を作製した。次いで、得られた急冷薄帯合金を1×10<sup>-2</sup>Pa以下の赤外線イメージ炉中において、750℃まで昇温し、約180秒間保持する条件で熱処理することにより、薄帯合金試料を得た。熱処理の昇温速度については、図12

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に示すように、室温（27℃）から $T_1$ まで180K/分、 $T_1$ から750℃（1023K）まで3K/分とし、 $T_1$ を27～750℃の範囲で試料毎に任意に変更することにより、種々の昇温速度で熱処理した薄帯合金試料を得た。更に、図13に示すように、室温（27℃）から $T_2$ まで3K/分、 $T_2$ から750℃まで180K/分とし、 $T_2$ を27～750℃の範囲で試料毎に任意に変更することにより、種々の昇温速度で熱処理した薄帯合金試料を得た。

【0063】急冷薄帯合金について、昇温速度を6～40K/分としてDSC測定（示差走査熱量測定）を行った。結果を図14に示す。いずれの昇温速度においても、500～650℃の範囲において、bcc-Fe相の結晶化による発熱ピークが確認される。また、650℃以上の温度範囲において、Nd<sub>2</sub>Fe<sub>14</sub>B相の結晶化による発熱ピークが確認される。

【0064】 $T_1$ を27～750℃の範囲で任意に変化させて得られた薄帯合金試料の残留磁化（ $I_r$ ）、角形比（ $I_r/I_s$ ）、保磁力（ $iH_c$ ）の $T_1$ の依存性を調べた結果を図15に示す。図15から明らかなように、 $T_1$ が500℃以下では、 $I_r$ 、 $I_r/I_s$ 、 $iH_c$ が低く、硬磁気特性が劣化していることがわかる。これは、図12から、 $T_1$ が500℃以下では、昇温速度3K/分の温度範囲の下限が500℃以下となり、bcc-Fe相の析出する温度範囲（500～650℃）で昇温速度が低くなるので、bcc-Fe相の発生核サイト数が減少し、結果的にbcc-Fe相及びbcc-Fe相の粒間から析出し成長するNd<sub>2</sub>Fe<sub>14</sub>B相の結晶粒径が大きくなり、交換結合性が低下して硬磁気特性が劣化したものと推定される。また、昇温速度3K/分の温度範囲が650～750℃の場合（ $T_1$ が650℃）では、Nd<sub>2</sub>Fe<sub>14</sub>B相の析出する温度範囲において昇温速度が低くなっている。Nd<sub>2</sub>Fe<sub>14</sub>B相の結晶粒の肥大化による交換結合性の低下が懸念されたが、実際には、得られた薄帯合金試料の硬磁気特性は図15に示すように良好であった。これは、速い昇温速度下でbcc-Fe相の結晶粒が既に数多く析出し、Nd<sub>2</sub>Fe<sub>14</sub>B相の析出するスペースが相対的に小さくなっているため、Nd<sub>2</sub>Fe<sub>14</sub>B相の析出の際の結晶粒の成長が抑制されたために、交換結合性が向上したためと推定される。

【0065】次に、 $T_2$ を27～750℃の範囲で任意に変化させて得られた薄帯合金試料の残留磁化（ $I_r$ ）、角形比（ $I_r/I_s$ ）、保磁力（ $iH_c$ ）の $T_2$ の依存性を調べた結果を図16に示す。図16から明らかなように、 $T_2$ が650℃以上では、残留磁化（ $I_r$ ）、角形比（ $I_r/I_s$ ）、保磁力（ $iH_c$ ）が低く、硬磁気特性が劣化していることがわかる。これは、図13から、 $T_2$ が650℃以上では、昇温速度3K/分の温度範囲の上限が650℃以上となり、bcc-

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Fe相の析出する温度範囲（500～650℃）での昇温速度が低くなるので、bcc-Fe相の結晶粒が肥大化し、Nd<sub>2</sub>Fe<sub>14</sub>B相との交換結合性が低下して硬磁気特性が劣化したものと推定される。

【0066】以上の結果から、組成が本発明の範囲であり、bcc-Fe相（初相）が析出する温度範囲内（500～650℃）において、昇温速度を10K/分以上とすることにより、硬磁気特性に優れた薄帯合金試料が得られることがわかる。

【0067】（実験例4）Fe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub>B<sub>5</sub>なる組成の急冷後の非晶質合金薄帯をアニール温度750℃で熱処理して得られた硬磁性材料の磁化の温度変化を調べた。また、Fe<sub>88</sub>Pr<sub>7</sub>B<sub>5</sub>なる組成の急冷後の非晶質合金薄帯をアニール温度650℃で熱処理して得られた硬磁性材料の磁化の温度変化を調べた。その結果を図17に示す。図17には、Fe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub>B<sub>5</sub>なる組成の硬磁性材料とFe<sub>88</sub>Pr<sub>7</sub>B<sub>5</sub>なる組成の硬磁性材料の磁化の温度変化を示す。図17に示されているように、温度の上昇とともに磁化は2ステップで減少している。このことから、硬磁性材料の磁化に参与する相が2相存在していることが認められる。また、315℃付近で磁化の減少の度合いが変化していることから、この付近がFe<sub>14</sub>Nd<sub>2</sub>B相のキュリー温度であり、770℃付近で磁化の減少の度合いが変化していることから、この付近がbcc-Fe相のキュリー温度であることが分る。なお、ここで非晶質相に起因する磁化のステップが見られないのは、磁化が低いことと体積分率が小さいことによるものと考えられる。

【0068】また、ここで得られたFe<sub>88</sub>Nb<sub>2</sub>Pr<sub>5</sub>B<sub>5</sub>なる組成の硬磁性材料とFe<sub>88</sub>Pr<sub>7</sub>B<sub>5</sub>なる組成の硬磁性材料の磁化曲線の第2象限を図18に示す。図18に示されているように、磁化曲線は、単一相からなる磁性材料と同様な、ステップの見られない磁化曲線となっており、微細なソフト磁性相とハード磁性相とが磁的に結合した交換結合磁石が得られていることが明らかである。

【0069】

【発明の効果】以上説明したように、本発明の硬磁性材料は、Fe、Co、Niのうち1種以上の元素Tと、希土類元素のうち1種以上からなる元素Rと、Bを含む合金からなり、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下であり、保磁力（ $iH_c$ ）が1kOe以上のものであるので、温度特性が優れており、センサ等に利用した場合に温度変化に起因する出力のドリフトを防止することができるので、検出精度の信頼性を向上させることができる。また、この硬磁性材料は、熱処理により析出した微細結晶質相のbcc-Fe相の平均結晶粒径が微細化しており、ソフト磁性相（bcc（体心立方構造）-Fe）とハード磁性相（R<sub>2</sub>Fe<sub>14</sub>B）の交換結

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合特性が向上しており、優れた硬磁気特性が得られる。さらに、この硬磁性材料は、希土類元素Rの含有量を少なくしても良好な硬磁気特性が得られるので、比較的低い製造コストで製造することができる。

【0070】また、本発明の硬磁性材料は、保磁力1kOe以下のソフト磁性相または準ハード磁性相と、保磁力1kOe以上のハード磁性相とをそれぞれ10vol(体積)%以上含む合金からなり、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下であり、保磁力が1kOe以上のものである。ソフト磁性相とハード磁性相のそれぞれの特性を兼ね備えることができ、また、低コストで、硬磁気特性が優れ、しかも温度特性が優れるという利点がある。また、本発明の硬磁性材料は、キュリー温度が600℃以上の磁性相とキュリー温度が600℃以下の磁性相とをそれぞれ10vol(体積)%以上含む合金からなり、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.15%/K以下であり、保磁力が1kOe以上のものである。ソフト磁性相とハード磁性相のそれぞれの特性を兼ね備えることができ、また、低コストで、硬磁気特性が優れ、しかも温度特性が優れるという利点がある。

【0071】本発明の硬磁性材料は、Fe、Co、Niのうち1種以上の元素Tと、希土類元素のうちの1種以上からなる元素Rと、Bとを含む合金からなり、保磁力の温度係数の絶対値が0.35%/K以下であり、保磁力が1kOe以上のものである。特に小型のセンサ等を使用した場合には、磁石がパーミアンス係数で2以下の形状となり、磁石の硬磁気特性は保磁力の温度係数に影響されることとなり、小型のセンサ等の温度変化に起因する出力のドリフトを防止することができるので、検出精度の信頼性を向上させることができる。

【0072】また、本発明の硬磁性材料は、保磁力1kOe以下のソフト磁性相と保磁力1kOe以上のハード磁性相とをそれぞれ10vol(体積)%以上含む合金からなり、保磁力の温度係数の絶対値が0.35%/K以下であり、保磁力が1kOe以上のものである。ソフト磁性相とハード磁性相の中間の特性を備えることができ、また、低コストで、硬磁気特性が優れ、しかも温度特性が優れるという利点がある。また、本発明の硬磁性材料は、キュリー温度が600℃以上の磁性相とキュリー温度が600℃以下の磁性相とをそれぞれ10vol(体積)%以上含む合金からなり、保磁力の温度係数の絶対値が0.35%/K以下であり、保磁力が1kOe以上のものである。ソフト磁性相とハード磁性相の中間の特性を備えることができ、また、低コストで、硬磁気特性が優れ、しかも温度特性が優れるという利点がある。

【0073】本発明に係る硬磁性材料において、平均結晶粒径100nm以下の微細結晶質相を主体として含む

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ものにあつては、特に、ソフト磁性相とハード磁性相の交換結合特性が優れ、硬磁気特性をより向上させることができる。また、本発明に係る硬磁性材料において、合金溶湯を急冷して得られた非晶質相を主相とする合金が熱処理されたものにあつては、低コストで、硬磁気特性が優れ、しかも温度特性が優れる硬磁性材料が好適に得られる。

【0074】本発明に係る硬磁性材料において、特に、上記の構成の合金溶湯を急冷して得られた非晶質相を主相とする合金が、少なくとも結晶質相の初相が析出する温度範囲において10K/分以上の昇温速度で熱処理されてなるものにあつては、bcc-Fe相の結晶粒が多数形成し、その結晶粒の肥大化を防ぐことができると共に、後から生成する $R_2Fe_{14}B$ 相の結晶粒の肥大化も防げるので、上記合金中に析出する微細結晶質相のbcc-Fe相と $R_2Fe_{14}B$ 相の平均結晶粒径を微細化することができる。また、 $R_2Fe_{14}B$ 相においては、粒径の昇温速度依存性はbcc-Fe相の場合よりも大きい。bcc-Fe相の結晶粒が $R_2Fe_{14}B$ 相が析出する以前に多数生成し、 $R_2Fe_{14}B$ 相が析出するスペースが小さくなっている。そのため、 $R_2Fe_{14}B$ 相の結晶粒の大きさは $R_2Fe_{14}B$ 相の析出する温度範囲での昇温速度によらず、初相(bcc-Fe相)の析出する温度範囲での昇温速度に依存している。即ち、 $R_2Fe_{14}B$ 相の結晶粒径は初相の析出する温度領域で高速昇温することにより微細化する。そのことにより、bcc-Fe相の結晶粒と $R_2Fe_{14}B$ 相の結晶粒との隣り合う確率が高くなり、ソフト磁性相(bcc(体心立方構造)-Fe)とハード磁性相( $R_2Fe_{14}B$ )の交換結合が行われ易くなるために交換結合特性が向上し、優れた硬磁気特性が得られる。

【0075】本発明に係る硬磁性材料において、パーミアンス係数が2以上となる形状で使用したときの磁化の温度係数の絶対値が0.10%/K以下としたものにあつては、特に、温度特性が優れる。また、本発明に係る硬磁性材料において、パーミアンス係数が10以上となる形状で使用したときの磁化の温度係数の絶対値が0.08%/K以下としたものにあつては、特に、温度特性が優れる。更に、本発明に係る硬磁性材料において、室温~100℃での保磁力の温度係数の絶対値が0.30%/K以下としたものにあつては、特に、温度特性が優れる。

【0076】本発明に係る硬磁性材料によれば、保磁力が2kOe以上の硬磁性材料を実現できる。また、本発明に係る硬磁性材料によれば、飽和磁化( $I_s$ )に対する残留磁化( $I_r$ )の割合( $I_r/I_s$ )が0.6以上の硬磁性材料を実現でき、従って、高い残留磁化( $I_r$ )を実現することができ、高い最大磁気エネルギー積( $(BH)_{max}$ )を持つ硬磁性材料を得ることができる。本発明の硬磁性材料にあつては、組成を $T_xMyR_z$



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Bwとし、組成比を示すx、y、z、wは原子%で、 $50 \leq x$ 、 $0 \leq y \leq 15$ 、 $3 \leq z \leq 20$ 、 $2 \leq w \leq 20$ なる関係を満足し、好ましくは $80 \leq x \leq 93$ 、 $1 \leq y \leq 5$ 、 $3 \leq z \leq 10$ 、 $3 \leq w \leq 7$ なる関係を満足し、より好ましくは $86 \leq x \leq 93$ 、 $1 \leq y \leq 3$ 、 $3 \leq z \leq 7$ 、 $3 \leq w \leq 5$ なる関係を満足することにより、かつ、残留磁化(Ir)が $100 \text{ emu/g}$ 以上のものとする事により、希土類元素の濃度が低くても良好な非晶質相が得られ、その後熱処理されることより硬磁気特性を付与する化合物が析出されるので、低コストで優れた硬磁気特性を有し、温度特性が優れた硬磁性材料が得られる。

【0077】本発明の硬磁性材料にあっては、組成を $T_xMyRzBwEv$ とし、組成比を示すx、y、z、w、vは原子%で、 $50 \leq x$ 、 $0 \leq y \leq 15$ 、 $3 \leq z \leq 20$ 、 $2 \leq w \leq 20$ 、 $0 \leq v \leq 10$ なる関係を満足するものとする事により、さらに、耐食性をも備えることができる。また、ここでの組成式中の組成比を示すx、y、z、w、vを原子%で、 $80 \leq x \leq 93$ 、 $1 \leq y \leq 5$ 、 $3 \leq z \leq 10$ 、 $3 \leq w \leq 7$ 、 $0 \leq v \leq 5$ 、より好ましくは $86 \leq x \leq 93$ 、 $1 \leq y \leq 3$ 、 $3 \leq z \leq 7$ 、 $3 \leq w \leq 5$ 、 $0.1 \leq v \leq 5$ なる関係を満足することにより、耐食性をも備えるうえ、より優れた硬磁気特性を得ることができる。本発明に係る硬磁性材料においては、Si元素がT元素置換で0.5～5原子%添加されることにより、あるいはT元素中にFe以外にCoが含まれることにより、温度特性をより向上させることができる。従って本発明の硬磁性材料にあっては、磁気式ロータリーエンコーダやポテンシオメータ、センサ、アクチュエータ、スピーカ、モータなどの各種の装置に使用される磁石材料として有用であり、製造コストの低減を図ることができる。

#### 【図面の簡単な説明】

【図1】 本発明の硬磁性材料をホールポテンシオメータ用磁石に適用した実施形態の例を示す斜視図である。

【図2】 本発明の硬磁性材料を磁気式ロータリーエンコーダ用磁石に適用した実施形態の例を示す斜視図である。

【図3】 本発明の硬磁性材料をスピーカ用磁石に適用した実施形態の第一の例を示す断面図である。

【図4】 本発明の硬磁性材料をスピーカ用磁石に適用した実施形態の第二の例を示す断面図である。

【図5】  $Fe_{76}Co_{10}Nb_2Pr_7B_5$ なる組成の薄帯合金試料の302.5K～489Kにおける減磁曲線(第2象限)を示すグラフである。

【図6】  $Fe_{66}Co_{20}Nb_2Pr_7B_5$ なる組成の薄帯

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合金試料の308K～471Kにおける減磁曲線(第2象限)を示すグラフである。

【図7】  $Fe_{84}Nb_2Pr_7B_5Si_2$ なる組成の薄帯合金試料の301.5K～477Kにおける減磁曲線(第2象限)を示すグラフである。

【図8】 実施例の薄帯合金試料ならびに比較例の磁石の磁気特性と温度との関係を示す図である。

【図9】 実施例の薄帯合金試料ならびに比較例の磁石をそれぞれ $p=1.5$ 、 $p=1.0$ となる形状で使用したときのIrの温度変化を示す図である。

【図10】 本発明の組成の範囲内にある焼結バルク(合金圧密体)、本発明の組成の範囲内にある薄帯合金ならびに従来のNd-Fe-B系磁石のパーミアンス係数と温度係数との関係を示す図である。

【図11】 本発明の組成の範囲内にある薄帯合金の温度(T)と保磁力(iHc)との関係を示すグラフである。

【図12】 昇温速度のパターンを説明するための図である。

【図13】 昇温速度のパターンを説明するための図である。

【図14】 急冷法により得られた $Fe_{88}Nb_2Nd_5B_5$ なる組成の非晶質合金薄帯試料の各昇温速度におけるDSC(示差走査熱量測定)曲線を示す図である。

【図15】  $Fe_{88}Nb_2Nd_5B_5$ なる組成の試料のIr、Ir/I<sub>s</sub>及びiHcのT<sub>1</sub>の依存性を示すグラフである。

【図16】  $Fe_{88}Nb_2Nd_5B_5$ なる組成の試料のIr、Ir/I<sub>s</sub>及びiHcのT<sub>2</sub>の依存性を示すグラフである。

【図17】  $Fe_{88}Nb_2Pr_5B_5$ なる組成の硬磁性材料と $Fe_{88}Pr_7B_5$ なる組成の硬磁性材料の磁化の温度変化を示すグラフである。

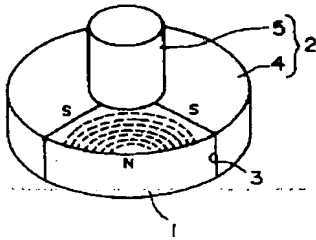
【図18】  $Fe_{88}Nb_2Pr_5B_5$ なる組成の硬磁性材料と $Fe_{88}Pr_7B_5$ なる組成の硬磁性材料の磁化曲線の第2象限を示すグラフである。

#### 【符号の説明】

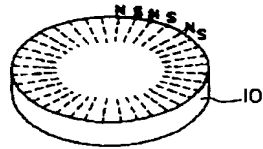
1…磁石部、2…支持部、3…切り欠き部、4…円盤部、5…接続部、10…ロータリーエンコーダ用磁石、21…ボールピース、22…圧粉磁心(ヨーク)、23、24…磁石、25…コーン状振動板、31、32…ボールピース、33…磁石、34…ヨーク、35…コーン状振動板、36…磁気シールドカバー、37…ボルト、38…ワッシャー、39…ナット。

(16)

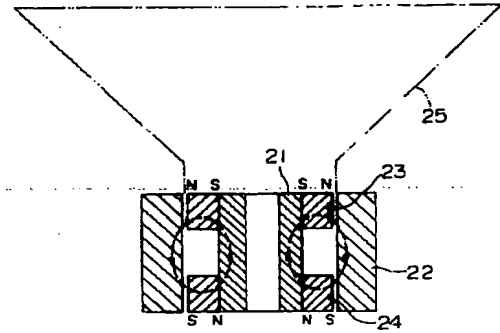
【図1】



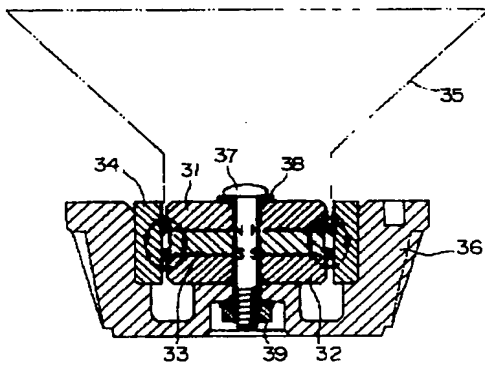
【図2】



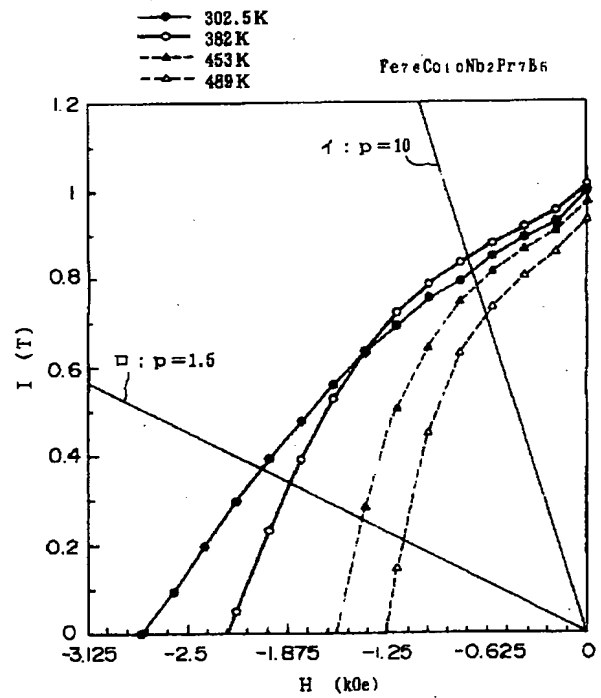
【図3】



【図4】

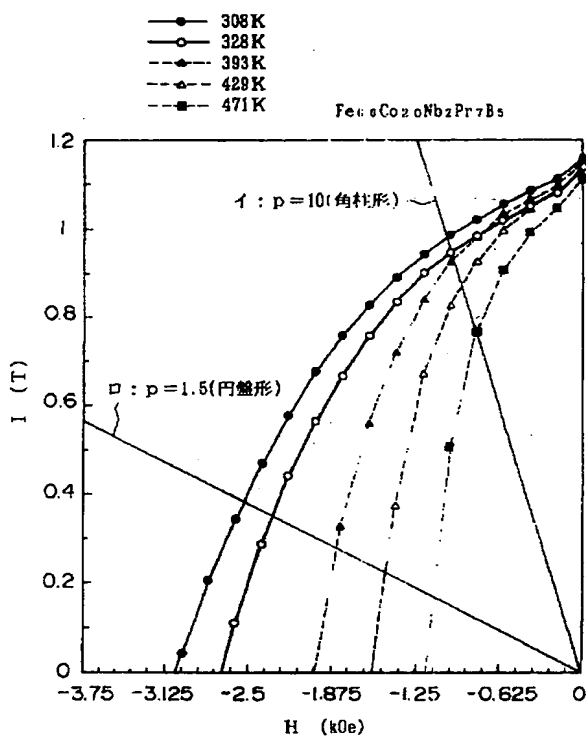


【図5】

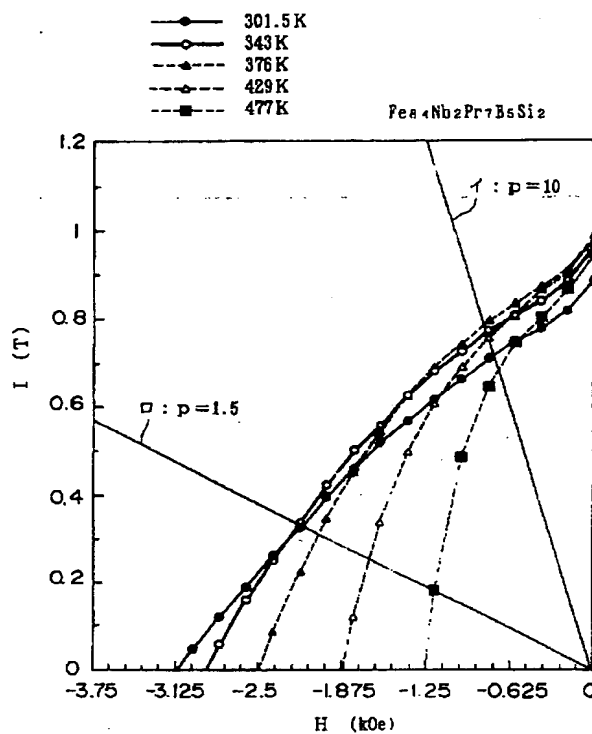


(17)

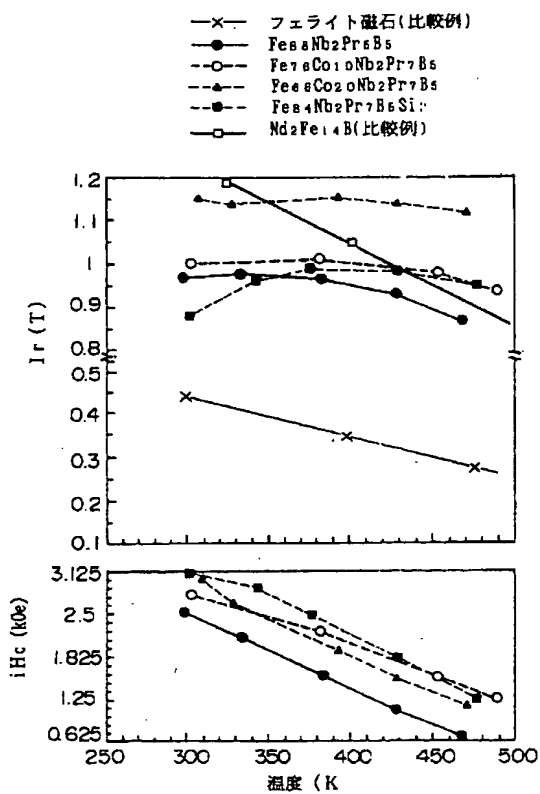
【図6】



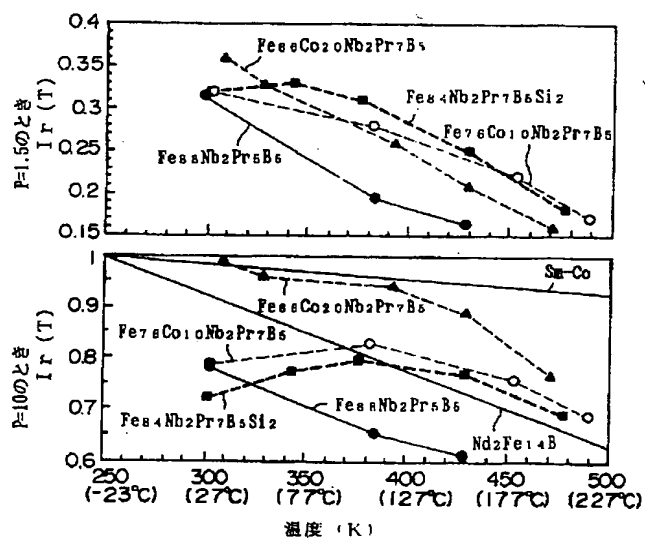
【図7】



【図8】

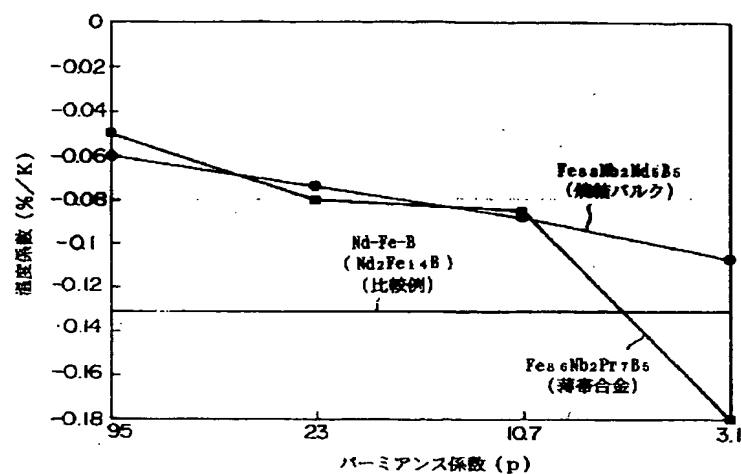


【図9】

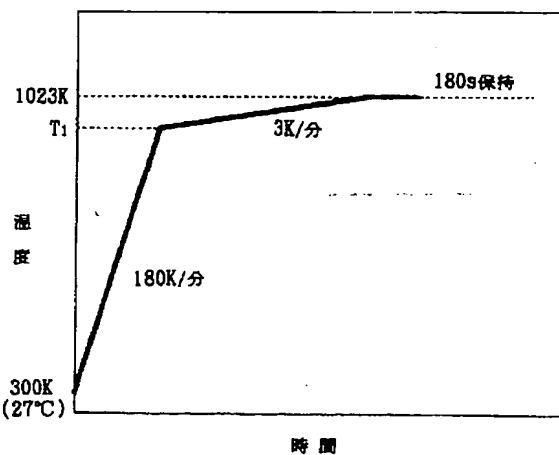


(18)

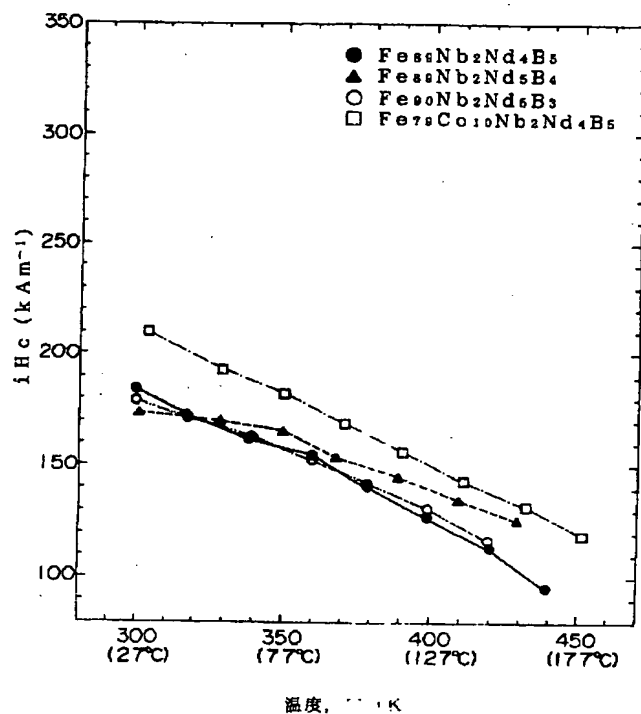
【図10】



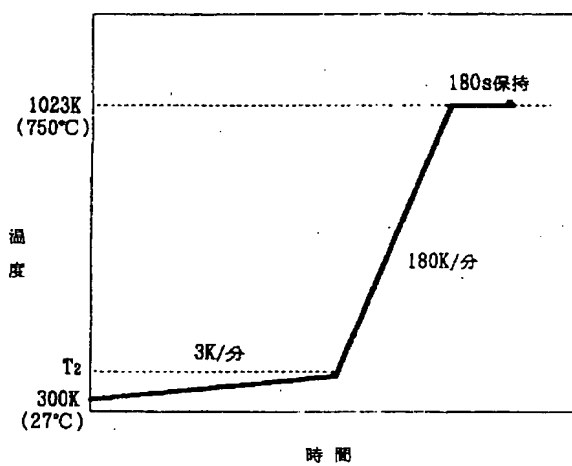
【図12】



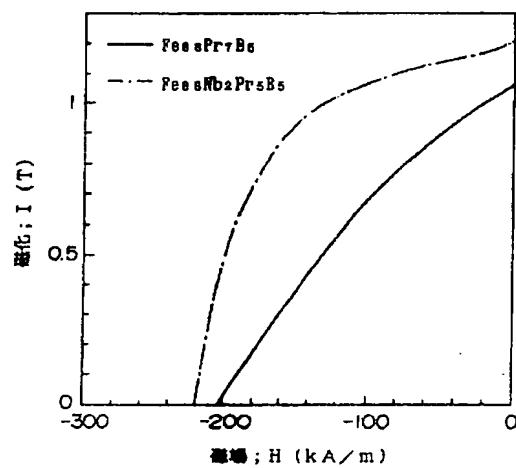
【図11】



【図13】

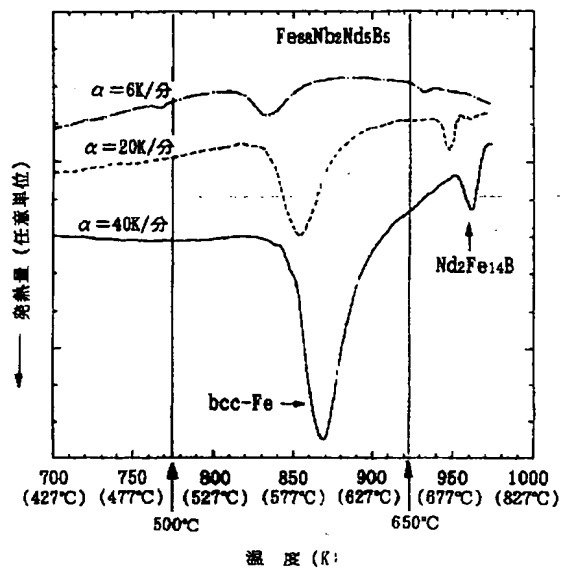


【図18】

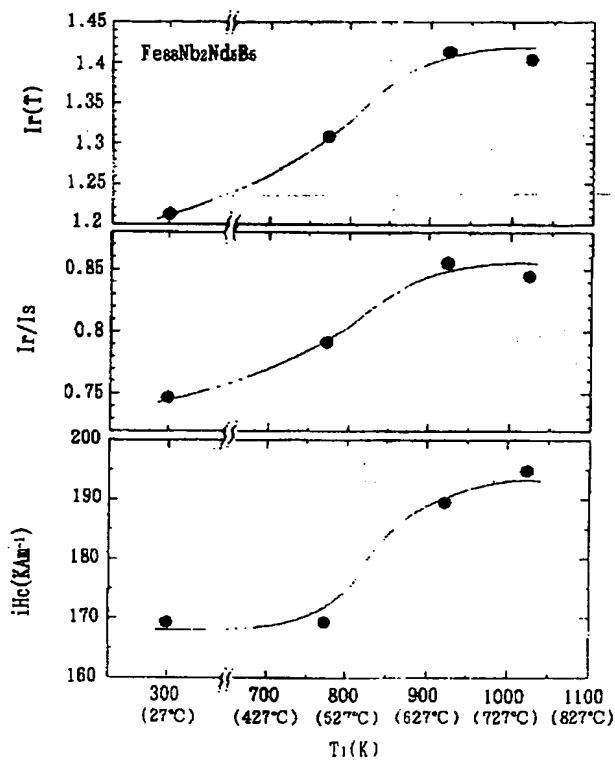


(19)

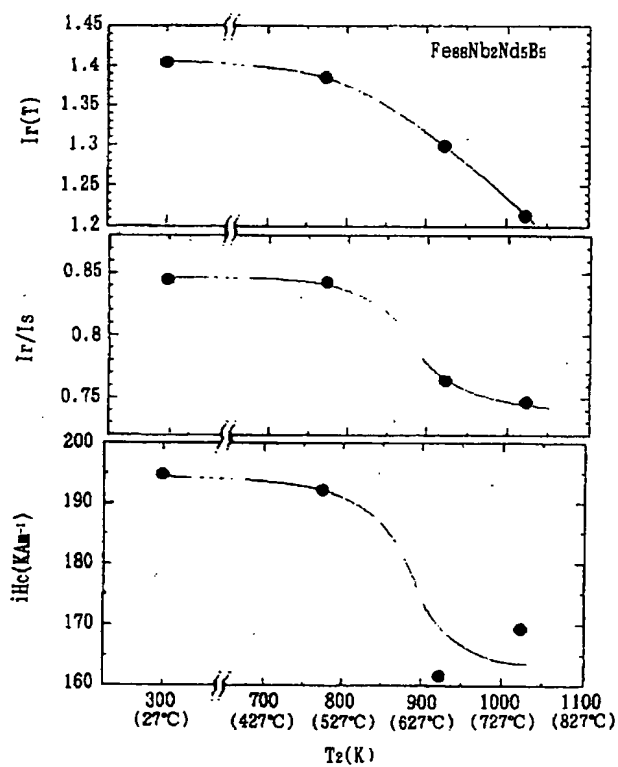
【図14】



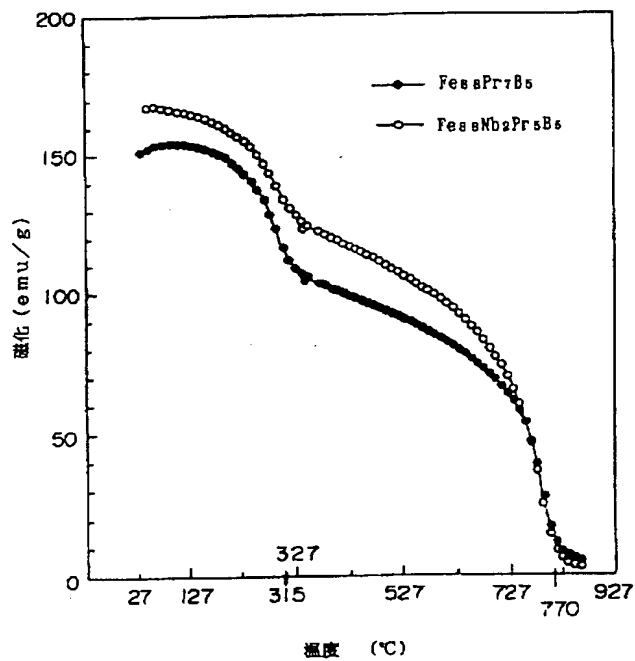
【図15】



【図16】



【図17】



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フロントページの続き

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